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MERCURY CELL BATTERY INVESTIGATION

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(Prepared under Contract No. AF 33(657)-7706
by the P. R. Mallory & Co., Inc., Indianapolis,
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FOREWORD

This report was prepared by P. R. Mallory & Co., Inc. Indianapolis, Indiana for the Aeronautical Systems Division of Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(657)-7706 under Task No. 817304-14 of Project No. 8173. It is our pleasure to acknowledge the assistance of Messrs. J. Cooper and W. Bishop, Project Engineers of the Aeronautical Systems Division.

This is a final report covering the period 15 December 1961 to 15 December 1962.

ABSTRACT

The rechargeable electrochemical system zinc/potassium hydroxide/mercuric oxide-silver has been investigated from the viewpoint of aerospace requirements. Individual study phases were used to evaluate cell components, both separately and as operating cells. Two versions of an exploratory research cell, with accompanying pellet type reference electrode, were successfully used during positive and negative electrode charge-discharge experiments.

Zinc anodes containing high percentages of mercury were discharged with efficiencies over 90% at rates up to 2000 ma/in² under uninhibited conditions. Reliable apparatus was developed to determine the gas volume generated during chemical reactivity rate studies between high mercury content anodes and electrolytes. The system of Zn-Hg-Ag was found to be quite compatible with electrolyte containing zincate. A cell cup retaining member for the high mercury-zinc alloy was fabricated and employed in completed cells. Discharge utilization obtained was comparable to that obtained in the research cell.

Results obtained during electrolyte additive studies were not encouraging.

A comprehensive study of separator materials was made. Electrical resistance, tensile strength, and metal ion content values were obtained on commercially available and specially prepared materials after various exposure periods.

Positive electrode densification experienced during cycle testing appears to be related to cycle depth. The additives which were investigated did not minimize the situation when electrodes were deep cycled. The use of palladium in the positive electrode alloy improved charge efficiency.

Automatic cycle testing equipment was used to accumulate data on the two hour simulated orbit cycle. Several preliminary test vehicle cells completed more than 1000 cycles. A ten cell series connected battery with controlled overall charging voltage, completed 300 cycles before the first failure occurred.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

TABLE OF CONTENTS

	Page
I. Introduction	1
II. Methods and Instrumentation	2
A. Chemical Reactivity Rate Studies	2
B. Exploratory Research Cell	4
C. Fabrication of Anode Retaining Member	5
D. Evaluation of Separator Materials	6
III. Factual Data and Discussions	8
A. Negative Electrode Study	8
1. Chemical Reactivity Rates	8
2. Discharge Experiments	9
B. Electrolyte Study	15
1. Effects of Inhibitors under Static Conditions	16
2. Effects of Inhibitors under Dynamic Conditions	16
C. Separator Study	17
1. Effects of Electrolyte on Separator Materials under Static Conditions	18
2. Stability of Separators in Completed Cells under Static Conditions	21
3. Stability of Separators in Cells under Dynamic Cycle Conditions	24
4. Modified Separator Materials	25
D. Positive Electrode Study	26
E. Experimental Fabrication and Cycle Testing	29
1. Test Vehicle #1	29
2. Test Vehicle #2	30
3. Cycle Testing of Individual Cells	30
4. Cycle Testing of Series Connected Cells	32
5. Cells with Liquid Anode Retainers	32
6. Environmental Testing	33
IV. Summary and Conclusions	34
V. Recommendations	34

LIST OF ILLUSTRATIONS

	Page
Figure 1 Reactivity Rate Apparatus-Method III	36
Figure 2 Glass Research Cell	37
Figure 3 Plastic Research Cell	38
Figure 4 Determination of Separator Resistance	39
Figure 5 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH Electrolyte	40
Figure 6 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-1% ZnO Electrolyte	41
Figure 7 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-2% ZnO Electrolyte	42
Figure 8 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-4% ZnO Electrolyte	43
Figure 9 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-6.25% ZnO Electrolyte	44
Figure 10 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-6.25% ZnO Electrolyte at 160°F	45
Figure 11 Consecutive Discharges of a Ag-HgO Electrode after a Charge Cycle of 85 Minutes at 128 ma/in ²	46
Figure 12 Effect of Increased Charge Rate	47
Figure 13 Effect of Palladium in the Positive Electrode	48
Figure 14 Positive Electrode with 0.3% Pd	49
Figure 15 Positive Electrode with 0.3% Pd and 1% Graphite	50
Figure 16 Positive Electrode with 0.3% Pd and 1% Wood Charcoal	51
Figure 17 Positive Electrode with 1% Activated Charcoal Containing 10% Pd	52
Figure 18 Positive Electrode with 1% Activated Charcoal	53
Figure 19 Positive Electrode with 0.3% Pd and 1% Activated Charcoal	54

LIST OF ILLUSTRATIONS (continued)

	Page
Figure 20 Positive Electrode with 1% Pd and 3% Polyethylene Oxide	55
Figure 21 Positive Electrode with 1% Pd-Reduced Particle Size	56
Figure 22 Positive Electrode with 1% Pd and 2% Polyethylene Oxide	57
Figure 23 Test Vehicle #2	58
Figure 24 Discharge Curve of Liquid Anode Cell	59

LIST OF TABLES

Table I	Negative Electrode Rate and Utilization Determinations- (High Mercury-Zinc Compositions vs. Solid Pure Zinc)	Page 10
Table II	Percent Utilization at Various Rates (ma/in ²) of Different Ratios of Zinc and Mercury in the Negative Electrode	10
Table III	Cycling Experiments with Research Cell	11
Table IV	Cycling Experiments with Research Cell	12
Table V	Cycling Experiments with Research Cell	12
Table VI	Cycling Experiments with Research Cell	13
Table VII	Cycling Experiments with Research Cell	13
Table VIII	Cycling Experiments with Research Cell	14
Table IX	Cycling Experiments with Research Cell	14
Table X	Cycling Experiments with Research Cell	14
Table XI	Reactivity of Granulated Zinc Containing 13% Mercury with 40% KOH Containing Various Inhibitors as Measured by Hydrogen Gas Evolution	16
Table XII	Room Temperature Electrical Resistance and Tensile Strength of Separator Materials after Exposure to 40% KOH-6.25% ZnO Electrolyte	19
Table XIII	Characteristics of Separators Exposed to Cell Electrodes Under Static Conditions	22
Table XIV	Characteristics of Separators Exposed to Cycle Conditions in Test Vehicle #2	24
Table XV	Room Temperature Electrical Resistance and Tensile Strength of Regular & Modified C-1 & C-2 Separator Materials after Exposure to Electrolytes	25
Table XVI	Consecutive Discharges of a Ag-HgO Electrode after a Charge Cycle of 85 minutes at 128 ma/in ²	27
Table XVII	Automatic Cycle Testing of Test Vehicle #2	31

I. INTRODUCTION

Aerospace applications for electrochemical rechargeable batteries require a high degree of capability for these devices, particularly when consideration is given to the large required number of cycles. Small size, low weight and broad operating temperature range also pose rather severe requirements. At the present state of the rechargeable battery art, there is no system presently known which will fulfill all of these requirements. However, in spite of the present limitations of virtually all electrochemical rechargeable systems, it is appreciated that the most logical means for converting and storing energy for earth orbiting satellites for many orbits could best be achieved by some electrochemical system coupled with solar energy conversion.

The P. R. Mallory Company submitted to the Aeronautical Systems Division a proposal in response to Purchase Request No. 127380, entitled "Mercury Cell Battery Investigation." As a result of this proposal, Contract No. AF 33(657)-7706 was awarded effective 15 December 1961.

The objective of this program is to provide design criteria for long life lightweight secondary batteries for military aerospace application through the investigation of the zinc/potassium hydroxide/mercuric oxide-silver electrochemical system. The applied research will include, but not be limited to, the following work: (a) investigation of means for increasing moderate (down to 32°F) temperature capability of the mercury cell battery, and (b) investigation to determine best methods to prevent growth of zinc crystals on the negative electrode. Some of the goals this program will be directed toward accomplishing are:

1. The batteries shall be capable of 20 ampere discharge for 35 minutes with voltage maintained at 27.5 volts \pm 1.5 volts.
2. Batteries will be capable of storing sufficient energy in 85 minutes to satisfy the requirements of (1) above.
3. The battery shall be capable of repeated cycling to a goal of 25,000 cycles while operating in a temperature range of 32°F to 160°F.
4. Minimum weight (goal: 11 pounds) and minimum volume should be considered.
5. Battery shall be capable of operation in any position, in zero gravity environment, in a vacuum of 10^{-9} mm of Hg, and without maintenance throughout its entire cycle life.

Accomplishments in each of the established research phases toward meeting the above goals are reported in subsequent sections of this report.

II. METHODS AND INSTRUMENTATION

A. Chemical Reactivity Rate Studies

Since chemical non-reactivity of the anode metal or amalgam with the electrolyte is an important factor in achieving a long life system, a study of methods and apparatus to accurately determine this factor was made. The most obvious method is to measure the volume of gas generated during a given test period.

While measuring gas volumes released by a chemical reaction, several variables must be considered. For instance, when small volumes are being measured, a change in the relationship between atmospheric pressure, volume, and temperature will have adverse effects. However, if a constant temperature is maintained and the void volume in the reaction chamber is small, the effects of atmospheric pressure changes are minimized. Also, there must be no leaks, or hydrogen diffusion through the joints, and if a large number of evaluations are to be made with the same equipment, it should be easily dismantled and reused.

During the course of this work four methods of measuring gas volumes released during static tests were investigated. These methods are described below.

1. Method I

The initial apparatus for measuring gas volume was rather conventional and consisted of a test tube fitted with a rubber stopper and a glass tube fabricated so the outlet terminated under water. A graduated tube was filled with water and inverted over the outlet. Gas evolution was measured by the displacement of water from the graduated tube. This type equipment is acceptable for rough screening investigations, but the accuracy is limited where low gas volumes are involved.

2. Method II

In the interest of providing a better seal of the measuring tube with the reaction chamber than that offered by a rubber stopper, several assemblies were made and used employing a ground joint seal. A small bore glass tube was fused to the male part of a tapered glass joint. The tube, bent in the form of a double "U", was fused to a 1 ml pipette at the outlet end. A pipette graduated in hundredths of a milliliter was employed. The female part of the ground joint was closed by fusion to provide a reaction chamber of about 5 ml. In use the "U" tube is filled with a liquid such as water and the specimen, with the electrolyte, is placed in the reaction chamber, the ground joint is closed. Polyisobutylene is used on the ground surfaces of the glass to effect a good seal and permit disassembly. A thin layer of oil is applied to the liquid in the graduated tube to prevent evaporation.

Although this represented an improvement over Method I in some respects, it had the following deficiencies: (1) as gas was liberated, it was subjected to increasing pressure as the fluid column height increased, and (2) the void volume was sufficiently large to cause abnormal changes in readings with changes in atmospheric pressure and temperature.

3. Method III

A third method of gas volume measurement was investigated. The reaction chamber and glass joint used were similar to those in Method II except that a vertical glass graduated column was fused directly to the male section of a ground joint affording a means to minimize internal volume. The gas volume was then measured by the rise of a small mercury globule seal in the graduated tube above the gas. It has been established that the seal made by a mercury column of only 0.03 ml volume in a clean 1 ml pipette will support the weight of the mercury. The Method III design is shown in Figure 1.

4. Method IV

For gas volumes less than 1 ml, Warburg Manometer type equipment was used. These manometers, normally used in biochemical research, are commercially available. The 0.3 ml gas volume in the 30 cm length offers high precision volume measurement. The total volume of 0.3 ml can be discharged from the manometer repeatedly and additional gas measured, if required by long term tests. These manometers were used in conjunction with a constant temperature bath for reactivity rate studies at elevated temperatures (160°F).

It was found during the early work that chemical reactivity rates could not be determined readily with a high degree of precision and reliability. One of the major causes for lack of precision in the first methods employed was the effect of changes in atmospheric pressure. Other factors contributing to lack of precision are (1) possible leaks in the apparatus and (2) temperature fluctuations. To minimize the effect of changes in atmospheric pressure, the Method III apparatus was modified to reduce the volume by extending a heavy wall capillary tube through to the lower extremity of the male part of the ground glass seal. This reduction in volume also minimized the effect of temperature changes.

The superiority of Method III over Methods I and II was obvious and it became evident that it also had advantages over Method IV mainly because of its greater freedom from the effects of atmospheric changes. In view of this, all these methods were abandoned with effort concentrated on the use of Method III. During the further evaluation and continued use of this method, inconsistencies were experienced. Frequently, after an initial rise in gas volume, a subsequent reduction to the starting value or even below same, was obtained. Reasons for this decrease in volume, including gas losses by chemical reaction, absorption, and permeation through the seal were investigated. The cause was traced to the chloroform used to dissolve the polyisobutylene sealant. More reliable data have been obtained during recent tests when a lower vapor pressure solvent was employed.

B. Exploratory Research Cell

The nature of the technical requirements of the contract, particularly with respect to cycle duration, and in the interest of conducting a multiplicity of experiments under closely controlled conditions, with a minimum amount of time, dictated the adoption of a specialized cell for the dynamic experiments.

The glass exploratory research cell shown in Figure 2 was designed and fabricated during the first quarter. The cell body was made of precision bore glass tubing of 0.551" diameter, allowing an electrode area of 0.235 in². A side arm was attached for easy insertion of a reference electrode. The negative electrode assembly, composed of a silver disc brazed to a threaded copper stud, was held in place by an "O" ring and plastic plug. The anode material was placed on the surface of the silver disc. The positive electrode was a porous pellet with contact lead passing through the upper plastic plug seal. The electrode spacing was adjusted by (1) the length of the upper plastic plug seal, (2) the thickness of the positive electrode, and (3) the overall length of the cell wall. This glass research cell was used for all uninhibited evaluations of both the positive and negative electrodes. (Uninhibited conditions are defined as an excess of available electrolyte and no separators between the electrodes).

While acceptable results were obtained with uninhibited cell conditions using the glass research cell, a redesign was necessitated when evaluations with close electrode spacings employing separators were attempted. It was found that the absolute electrode separation required to prevent internal short circuits could not be maintained in the straight-walled glass cell, nor was it easy to obtain precise electrode spacing. A cross-section of the modified cell fabricated for close electrode studies is shown in Figure 3.

Spacer rings for controlled electrode spacing and positive clamping of separators between electrodes were incorporated in the new design. Electrode area remains unchanged from the glass cell (0.235 in²). The lower plastic plug seal can be modified to accommodate various negative electrode contacts. Provision for the reference electrode was made by drilling a hole in the cell wall.

The plastic modification allows experiments under closely controlled conditions by assuring proper separator positioning and definite electrode spacing.

An important part of the development of these research cells was that of the reference electrode. Although the Hg-HgO electrode is satisfactory with respect to reliable and reproducible measurements, it has disadvantages from the handling standpoint due to the liquid mercury. A small, simple, rigid electrode mounted on the end of a wire is highly desirable from the standpoints of handling ease and speed of measurements. To achieve this, an investigation of the Ag-Ag₂O electrode was made. This type of electrode was produced by the simple expedient of pressing silver powder containing 1.5% Ag₂O around the end of a silver wire. This electrode was stable against a Hg-HgO electrode in KOH electrolyte to within 1 millivolt

for about 20 hours, however, upon prolonged stand a considerable change was experienced. This change was as much as 110 millivolts in 111 hours at room temperature.

Another approach to the rigid reference electrode was undertaken with the system Ag-Hg-HgO. This was made by pressing 0.06 grams of Ag (31%) - Hg (69%) amalgam powder containing 2% HgO around the end of a silver wire. Stability measurements at ambient room temperature during several weeks in KOH indicate this electrode to be 13 ± 4 millivolts positive with respect to the Hg-HgO potential. Deviation from the Hg-HgO value is probably due to the presence of the silver and to the temperature coefficient of both electrodes. Also as a part of these stability evaluations an electrode was subjected to continuous discharge at 0.16 microamperes for 125 hours. (This current drain is approximately equivalent to that of a 10-11 megohm input impedance vacuum tube voltmeter). During this test period, the temperature range was 17.5°C to 28°C. A total change of 11 millivolts was encountered with 10 millivolts change occurring during the first 50 hours and 1 millivolt change during the final 75 hours.

Instrumentation with a direct current voltage source and an appropriate resistor-switch circuit was assembled for use with the research cells. This equipment was designed to charge two (2) cells while discharging one (1) cell because of the 85 minute charge time and 35 minute discharge time. A positive, negative, and reference electrode lead from each cell was plugged into the switch circuit to allow voltage readings between the positive and negative electrodes, the positive and reference electrodes, and the negative and reference electrodes on both the charge and discharge cycle. Rapid voltage measurements of sufficient precision were made with a Hewlett-Packard 412A instrument which will indicate 1 mv full scale. A variable load resistor for cell discharge and milliammeter for reading both the charge and discharge current are also included.

The exploratory research cell in conjunction with the reference electrode and the instrumentation described has been used in the exploratory work to measure the significant parameters of the various experimental cell members. Results from these investigations have guided the work associated with the extended cycle testing in larger cells.

C. Fabrication of Anode Retaining Member

After obtaining encouraging results with the high mercury-zinc negative electrode under uninhibited cell conditions during the early phases of the contract, effort was initiated during the second quarter on methods to fabricate a retaining member. The initial work was toward a design for use in the research cell where evaluations could be carried out more readily. The approach was to produce this member as a compartmented or open cellular structure, each cell being 0.125" x 0.125" x 0.062" deep and having walls 0.015" thick. In order to insure confinement of an equal amount of amalgam in each cell, there can be no cracks or fissures in the walls and the edges of same must be relatively smooth and even to effect a reasonable good closure of each cell by an electrolyte permeable member.

The best choice of material for the anode amalgam retaining member appears to be silver. Three methods have been used in attempts to fabricate the part. The first was to press silver powder in a steel die having the required configuration. Upon removal from the die, the pressed powder member was subsequently sintered to close the porosity and increase the strength. This method was found to have the following shortcomings: (1) difficulty in removing from the die without breakage due to low strength in the as-pressed condition and (2) the sintering operation produced abnormal shrinkage and cracking.

The second method was to cold form the member by high pressure pressing with a steel die. Although moderate success was achieved by this method, difficulty was encountered during the forming operation due to the work hardening characteristics of silver. Relief from this factor was sought by pressing at elevated temperatures to maintain the silver in a softer condition but loss of die strength and oxidation of same was encountered. While further attempts by this method using improved die materials or other impact techniques undoubtedly would have yielded satisfactory specimens for use in the research cells, the fabrication of larger members for advanced cycle testing vehicles would have required additional improvements and equipment not readily available. Consequently, this approach was abandoned.

The third and most successful method has been used to produce retainers for use in both the exploratory research cell and the larger (2.3" diameter) cycle test vehicle. This approach has involved melting the silver in an iron mold of the required configuration in a reduced pressure hydrogen atmosphere of about 1 mm. The mold was then removed from the silver by dissolution in hydrochloric acid or ferric chloride. Very precise and satisfactory retainers with cell dimensions of 0.125" x 0.125" x 0.125" deep and walls 0.010" thick have been obtained by this method.

D. Evaluation of Separator Materials

Accurate electrical resistance measurements of conductive separators in electrolytes are rather difficult to make. Several techniques have been described in the literature employing modified conductivity cells and both alternating and direct current for voltage drop measurements. Alternating current is chosen when possible because it prevents polarization of the electrodes, however, polarization with direct current can also be eliminated, or at least reduced to an insignificant value, by using chargeable electrodes.

Direct current methods of resistance measurement were evaluated and used during the early phases of this work. A conductivity cell employing mercuric oxide chargeable electrodes and 40% KOH-6.25% ZnO electrolyte was used. It was considered that resistance measurements made while charging current passed through the cell would be near normal separator operating conditions.

A plastic cell was constructed to provide for easy removal of the positive and negative electrodes which were spaced about 1-1/2" apart and having provisions for placement of the separator specimen midway between the electrodes. A capillary tube, connected

to a reference electrode, was positioned on each side of the separator. The capillary tips were positioned 0.1" apart.

A cell constant was established by measuring the voltage drop between the reference electrodes with one (1) ampere charging current flowing. At this one ampere current, according to Ohm's Law, the cell constant is equivalent to the voltage drop expressed in ohms. This measurement is repeated with the separator in place to obtain the additional voltage drop due to its resistance. The cell constant is subtracted from the measured resistance to obtain the resistance due to the separator. This total resistance multiplied by the exposed separator area (square inches) gives the areal resistance value in ohms-in².

Difficulty in making reliable and reproducible measurements was experienced with the d-c method described above, consequently, alternating current methods were investigated. One approach employed a-c with depolarized electrodes (anodized silver) in intimate contact with the electrolyte-wetted separator specimen. By this method, the resistance values were found to vary with frequency of the alternating current. The capacitive-reactance effect at the electrodes was quite pronounced at low frequencies giving rise to high resistance values. However, above 20 kc the measured values of resistance were comparable to those obtained by other methods. Although this method may have some merit in that no reference electrodes are required and that small areas of separators could be measured, it offered no outstanding advantages over other a-c methods.

The previously described d-c method was converted to a-c. (see Figure 4) To accomplish this, only minor modifications in the plastic cell described earlier were required. The capillary tubes and reference electrodes were replaced with platinum wires for measuring voltage drop, and the separator area exposed for measurement was decreased to 0.25 in². The cell constant and the voltage drop due to the separator was established at current values of 10 ma and 100 ma, otherwise the procedure and calculations were carried out as described for the d-c method.

The alternating current employed was 1000 cps from a Hewlett-Packard Model 201C audio oscillator. Current measurements were obtained by the voltage drop across a 100 ohm resistor indicated on a Ballantine a-c voltmeter. Cell voltage measurements were made with a Hewlett-Packard Model 400H a-c voltmeter having a minimum indication of 0.01 mv on the 1 mv scale.

The other two characteristics of separators investigated during this program were (1) metal content and (2) tensile strength. The chemical analysis for silver and mercury metal content was accomplished as follows: The material was dissolved in nitric acid and diluted in a volumetric flask. Two aliquots were used - one was titrated with ammonium thiocyanate solution for total silver plus mercury and the other was used to determine silver by the chloride gravimetric method. The amount of silver can then be subtracted from the silver plus mercury titration to give the mercury content.

Standard low range tensile test equipment and techniques were used to measure the strength of separator materials. The electrolyte-wetted tensile specimen was cut from a 2.156" diameter disc by trimming around a template. The rupture section was 0.4" wide and the cross section depends on the material thickness. Rubber covered eccentric rollers which tighten with increasing tension hold the specimen in a Dillon Universal Tester, Model L. The lowest range of the 0-300 pound capacity unit is 0-25 pounds, with scale divisions of 0.05 pounds.

III. FACTUAL DATA AND DISCUSSIONS

A. Negative Electrode Study

It is generally known that the behavior of a conventional zinc anode operating reversibly in an alkaline electrolyte is quite unpredictable and difficult to control. This is largely attributable to the dual manner in which it operates. During the discharge part of the cycle there is initially a dissolution reaction to form soluble zincate ions, followed by the formation of zinc oxide on the surface of the anode. During the charge part of the cycle, the oxide is reduced to metal having a spongy texture followed by an electrodeposition process discharging zinc ions from the solution to deposit metal onto the spongy surface. These charging processes coupled with the crystal habit of zinc produces an acicular or dendritic structure on the surface of the anode. With successive cycling, this condition is enhanced to a point where the projections reach the cathode to cause a short circuit. Efforts to control this phenomenon by means of separators have only been partially successful.

To circumvent this deleterious behavior of the solid zinc anode, one approach is to employ this member in a liquid or at least a partly liquid state with mercury. This concept would provide a condition whereby zinc oxide reduced to metal or zinc deposited from the solution during charge would become entrapped by the liquid amalgam, thus minimizing or eliminating a dendritic type of growth. Previous investigations have indicated this approach to be valid and if proven successful from the physical and electrochemical standpoints, it would contribute greatly to long cycle life. The exploitation of this concept requires two major areas of investigation. One is the study of reactivity between the various amalgam compositions and the electrolyte and the other is the determination of the rate characteristics.

1. Chemical Reactivity Rates

Since chemical non-reactivity of the anode metal or amalgam with the electrolyte is an important factor in achieving a long-life system, precise methods of determining this are highly important. The usual method employed is to determine the amount of hydrogen gas liberated over a period of time. This method is basically good, however, several factors must be brought under control in the

apparatus used in order to achieve the required precision. (See Methods and Instrumentation section).

Reactivity rates involve the factors of (a) purity of the anode metal, (b) temperature, (c) purity of the electrolyte, (d) presence or absence of zincate in the electrolyte, and (e) physical state of the anode metal whether liquid or solid, and perhaps others. Representative chemical reactivity rate data, which were obtained after Method III modifications were completed, will be presented.

Toward determining the effect of the liquid anode retaining metal on the reactivity rate of the amalgam with the electrolyte, silver foil having an approximate area of 1 square inch was coated with 5% Zn-95% Hg amalgam and exposed to electrolyte. Samples were placed in 40% KOH electrolyte and in 40% KOH electrolytes containing 1%, 2%, 4%, and 6.25% ZnO, respectively, at room temperature and in 40% KOH-6.25% ZnO electrolyte at 160°F. The gas volume recorded, along with the temperature and atmospheric pressure, is shown in Figure 5 through Figure 10. It will be observed that a combined low temperature and high pressure produced a decrease in indicated gas volume simultaneously. The larger gas volume obtained in the 40% KOH electrolyte points to the requirement of zincate in the electrolyte for extended life. This low reactivity, as measured by gas evolution, proves rather conclusively the compatibility of the metal system, Ag-Hg-Zn, with KOH electrolyte containing zincate.

2. Discharge Experiments

Based on the technical requirements of this project, it was originally calculated that if the electrodes would sustain a rate of 300 ma/in², a battery would eventually result having a satisfactory geometrical configuration. With this as a design goal or "benchmark" and from previous experience with anodes having a weight proportion of zinc in mercury in the range of 25-50%, experiments were started with Zn contents in lower ranges. The object here was not only to determine the initial rate capabilities of a given composition, but also to determine the effect of the diminishing concentration of zinc. These experiments were made under conditions of quite uninhibited cell operation in that there was an excess of electrolyte, an excess of area and capacity of HgO depolarizer, and no separators between the electrodes. This arrangement was used toward making the anode the rate-limiting member in order to find its maximum permissible rate before the on-set of polarization.

Using the exploratory research cell having electrodes of 0.235 in² area and a spacing of 0.25", three zinc-amalgam anode compositions were examined. They were 10%, 5%, and 2% zinc, balance mercury. In each case, the zinc content was 0.1 gram (equivalent to 82 ma-hrs). This is 100% in excess of the capacity required for this electrode area at a discharge rate of 300 ma/in² on the simulated two hour orbit. First experiments with these amalgam compositions gave virtually 100% utilization at the 300 ma/in² rate. Data given in Table I are at the 600 ma/in² rate, compared

with the performance of a 99.99% pure solid zinc electrode weighing approximately 1 gram. Determinations were made at room temperature and at a constant rate of discharge.

TABLE I

Negative Electrode Rate and Utilization Determinations-
(High Mercury - Zinc Compositions vs. Solid Pure Zinc)

<u>Anode Composition</u>	<u>Current Density (ma/in²)</u>	<u>Time (Minutes)</u>	<u>Capacity (ma-hrs)</u>	<u>Utilization (%)</u>
10 Zn-90 Hg	600	34.7	81	99
5 Zn-95 Hg	600	34.75	81.2	99.1
2 Zn-98 Hg	600	34.5	80.5	98.3
Solid Zinc	213	34.2	28.5	(Polarized)
" "	300	17.5	20.5	(Polarized)
" "	450	7.4	13.0	(Polarized)
" "	600	4.8	11.2	(Polarized)

Additional evaluations, under the above cell conditions, by successive discharge and charge cycles up to and including two amperes per square inch discharge rate were made where the depolarizer was not the rate limiting electrode. Five zinc-amalgam anode compositions, namely, 5%, 10%, 15%, 20%, and 25% zinc, balance mercury were examined. In each case the zinc content was 0.1 gram. The percentage utilization data presented in Table II are based on the 82 ma-hr capacity of the anode. The capacity restored during each charge cycle was equivalent to the amount discharged, thus maintaining the 82 ma-hr base value. The charge rate of 247 ma/in² used is the charge requirement for a 600ma/in² discharge rate in a 2 hour orbit of 35 minutes discharge, 85 minutes charge. Determinations were made at ambient room temperature and at a constant rate of discharge and charge.

TABLE II

Percent Utilization at Various Rates (ma/in²) of Different Ratios
of Zinc and Mercury in the Negative Electrode

<u>Anode Composition</u>	<u>(ma/in²)</u>							
	<u>600</u>	<u>800</u>	<u>1000</u>	<u>1200</u>	<u>1400</u>	<u>1600</u>	<u>1800</u>	<u>2000</u>
5 Zn-95 Hg	99.7	98.6	98.1	97.9	95.1	94.7	95.1	94.6
10 Zn-90 Hg	92.2	98.5	99.1	95.7	94.2	93.0	92.5	---
15 Zn-85 Hg	95.1	94.0	93.5	90.4	91.3	93.7	93.2	93.9
20 Zn-80 Hg	87.5	88.5	92.6	93.7	93.0	89.2	92.4	92.3
25 Zn-75 Hg	95.0	95.4	90.7	96.3	94.9	95.4	92.1	91.7

From the above data, it is apparent the high mercury content anode will sustain a high discharge rate with excellent utilization at least under uninhibited conditions. It is also apparent that the rate sustaining capability of solid zinc is much below that of the high mercury anode.

The discharge experiments with the high mercury content anodes previously described were under conditions which permitted the anode to operate in an uninhibited manner in that no spacers were employed and ample free electrolyte was present thus permitting high discharge rates.

Experiments were directed toward ascertaining the rate capability of anodes in the compartmented anode retainers where various separator materials were employed along with closer electrode spacings and consequently a diminished amount of electrolyte. Representative data contained in Tables III through VII were obtained with the plastic research cell described in the Methods and Instrumentation section. In addition to the use of separator materials and a reduced volume of electrolyte, the effect of reducing the amount of anode amalgam from 82 ma-hrs to 41 ma-hrs was evaluated. Also a 50% reduction in the volume of the anode retainer cells was employed without reducing the amount of anode amalgam over that previously used. In these experiments the electrodes were recharged after each discharge operation to the extent of the preceding discharge capacity. It will also be noted that in all cases a constant charge rate was employed proportional to the preceding discharge rate according to the ratio of the specified orbit cycle, namely, 35 minutes discharge and 85 minutes charge.

In Table III the data will indicate the anode discharge efficiency at 300 ma/in² and 600 ma/in² when the electrodes were spaced 0.062" and with three separators between the electrodes, namely a 0.004" thick non-woven absorbent-separator next to the depolarizer, a 0.040" cellulosic absorbent-separator next to the anode, and 0.004" thick negative electrode barrier-separator interposed between these two. Although reasonably good performance was obtained at the 300 ma/in² discharge rate, the performance was considerably lower at the 600 ma/in² rate.

TABLE III

Cycling Experiments with Research Cell

Cycle No.	Discharge				Charge		
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Efficiency (%)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)
1	300	55.5	64.6	78.8	123.5	133.6	64.6
2	600	19.0	44.2	54.0	247	45.8	44.2
3	600	19.5	45.5	55.5	247	47.0	45.5
4	600	19.3	44.9	54.7	247	46.5	44.9

In Table IV discharge data at the 300 ma/in² and 600 ma/in² rates are given with electrode spacing reduced to 0.032" by substituting a thinner plastic spacer and also a thinner cellulosic absorbent-separator member. It will be noted that the performance is indicated to be slightly inferior at the 300 ma/in² rate and slightly better at the 600 ma/in² discharge rate, compared with the data obtained where the electrode spacing was 0.062".

TABLE IV

Cycling Experiments with Research Cell

Cycle no.	Discharge				Charge		
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Efficiency (%)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)
1	300	49.0	57.1	69.6	123.5	118.2	57.1
2	600	22.3	51.9	63.3	247	53.7	51.9
3	600	21.7	50.5	61.6			

In Table V is presented discharge data for a cell also having 0.032" electrode spacing with similar spacer arrangement. The essential deviation in this experiment was a 50% reduction in the depth of the compartments in the liquid anode container (0.031" instead of 0.062"). With this reduced volume in the anode container but with the usual amount of anode amalgam, namely 82 ma-hrs, the compartments of the anode container were full of zinc-mercury amalgam thus leaving no free space for electrolyte. A severe impairment in anode performance will be noted.

TABLE V

Cycling Experiments with Research Cell

Cycle No.	Discharge				Charge		
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Efficiency (%)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)
1	300	6.5	7.6	9.2	123.5	15.6	7.6
2	300	12.0	14.0	17.0	123.5	26.0	14.0
3	300	13.9	16.1	19.6	123.5	33.3	16.1
4	300	17.5	20.4	24.8	123.5	42.0	20.4
5	300	21.4	24.9	30.3	123.5	51.5	24.9
6	300	27.3	31.9	38.9	123.5	66.0	31.9
7	600	14.1	33.0	40.2			

In Table VI, data are given where the electrode spacing was reduced to 0.016" by use of a 0.004" absorbent-separator next to the depolarizer, a 0.008" cellulose absorbent-separator next to the anode, and a 0.004" regenerated cellulose barrier-separator member interposed between these two. The amount of anode amalgam was reduced to 41 ma-hrs from the usual

82 ma-hrs. Most of the discharge data was obtained at the 600 ma/in² rate. An increase in anode efficiency, even at the higher rate and closer electrode spacing, was obtained over that reported in Table V. This is probably attributable to the increased amount of the electrolyte contained in the compartments of the liquid anode container because less anode amalgam was employed.

TABLE VI

Cycling Experiments with Research Cell

Cycle No.	Discharge				Charge		
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Efficiency (%)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)
1	300	19.8	23.0	56.0	123.5	47.6	23.0
2	600	8.1	18.8	45.9	247	19.4	18.8
3	600	9.8	22.7	55.3	247	23.4	22.7
4	600	11.3	26.3	64.1	247	27.2	26.3
5	600	10.0	23.4	57.0			

The data in Table VII were obtained largely as a duplication of the experiments reported in Table VI, except the amount of amalgam was increased to the usual 82 ma-hrs thus excluding some electrolyte from the anode retainer. The reduced efficiency may be attributed to this.

TABLE VII

Cycling Experiments with Research Cell

Cycle No.	Discharge				Charge		
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Efficiency (%)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)
1	300	20.4	23.8	29.0	123.5	49.2	23.8
2	600	11.0	25.6	31.2	247	26.5	25.6
3	600	8.2	19.0	22.8	247	19.8	19.0
4	600	10.2	23.7	28.9			

For comparative purposes similar discharge experiments were made in the research cell except the anode was added to the compartmented retainer as a paste of ZnO and electrolyte (40% KOH-6.25% ZnO) and reduced to Zn by the charging operation. The electrode spacing was 0.016" with a 0.004" absorbent-separator next to the depolarizer, a 0.008" cellulose absorbent-separator next to the anode, and a 0.004" regenerated cellulose barrier-separator interposed between these two. In all cases an initial charge at 123.5 ma/in² to produce 82 ma-hrs capacity was employed. Discharge data are presented in Tables VIII, IX, and X.

The data in Table VIII were obtained with a deep (0.062") liquid anode container filled with ZnO-electrolyte paste prior to charging. The ZnO content, when charged, would be equivalent to 161 ma-hrs.

TABLE VIII

Cycling Experiments with Research Cell

Cycle No.	Charge			Discharge			Efficiency (%)
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	
1	123.5	169.6	82	300	53.2	62.6	76.3
2	123.5	129.6	62.6	600	5.1	12.9	15.7
3	123.5	26.3	12.9	600	12.5	29.1	35.5
4	247	30.0	29.1	300	35.3	41.2	50.2

In Table IX is presented data for a cell in which a shallow (0.031" instead of 0.062") liquid anode container was employed. The ZnO contained when charged, would be equivalent to 95 ma-hrs.

TABLE IX

Cycling Experiments with Research Cell

Cycle No.	Charge			Discharge			Efficiency (%)
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	
1	123.5	169.6	82	300	40.0	46.6	56.8
2	123.5	96.6	46.6	600	16.7	38.9	48.6
3	247	40.2	38.9	600	16.2	37.9	46.2
4	247	39.1	37.7	600	14.5	33.9	41.3

The data in Table X were a duplication of the Table IX experiment except the electrolyte content of the paste was reduced to obtain ZnO in the anode retainer equivalent to 110 ma-hrs if completely charged.

TABLE X

Cycling Experiments with Research Cell

Cycle No.	Charge			Discharge			Efficiency (%)
	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	Rate (ma/in ²)	Time (Min.)	Capacity (ma-hrs)	
1	123.5	169.6	82	300	54.0	63.0	76.8
2	123.5	130.3	63.0	600	22.1	51.4	62.9
3	247	54.0	51.4	600	21.4	48.3	58.9
4	247	49.9	48.3	300	46.4	54.1	65.9
5	123.5	111.9	54.1	600	17.4	40.5	49.3

Only cursory low temperature evaluations were made with the high mercury content anode. A 10% Zn-90% Hg anode was discharged and charged at 32°F in the exploratory research cell under the uninhibited conditions described earlier. Using 40% KOH-6.25% ZnO electrolyte utilization of over 95% was obtained at discharge rates 300 through 550 ma/in², but the low temperature effect was quite pronounced at 600 ma/in² when two cycles gave only 11.4% and 26.2% utilization. Performances somewhat lower were obtained under identical conditions when 35% KOH-5.5% ZnO type electrolyte was used. These cursory tests indicate the electrolyte best suited for use with the high mercury content anode for the temperature range down to 32°F will be fairly high in KOH content to improve anode reaction product solubility.

B. Electrolyte Study

The behavior of the anode in the zinc-mercuric oxide alkaline rechargeable cell is dependent upon the nature of the electrolyte. Perhaps one of the most complicating factors of this system is the fact that zinc, being an amphoteric metal, is soluble in KOH, both chemically and electrochemically, to a certain extent to form potassium zincate. The presence of zincate has both beneficial and detrimental effects. Due to the common ion effect, its presence virtually precludes chemical dissolution of the zinc by the electrolyte. When the electrolyte is devoid of the zincate ion, zinc is attacked by the electrolyte to liberate hydrogen gas and form potassium zincate (K₂ZnO₂). This evolution of gas is extremely detrimental in sealed batteries.

Zincate in the electrolyte has one detrimental effect in that it increases the resistivity of the electrolyte slightly. This becomes noticeable at the high rates of cell discharge and especially at low temperatures. In addition to the effect on the electrolyte resistance, the zincate ion precludes one of the anode reactions, namely the dissolution of zinc to form potassium zincate thus leaving the remaining possible reaction, the formation of zinc hydroxide (Zn(OH)₂) or zinc oxide (ZnO) on the surface. These being solid materials, they tend to limit the anode reaction rate by hindering the accessibility of the electrolyte to the anode surface thus giving rise to anode polarization.

Considering the secondary cell reactions, where the discharged anode must be electrochemically reconstituted by a "charging process", the presence of zincate in the electrolyte may be beneficial in certain respects. It affords two reactions to go on simultaneously, namely, the reduction of zinc oxide and/or zinc hydroxide on the surface of the anode and the electrodeposition of zinc from the solution. Although this electrodeposition process contributes to the charging rate, it has the shortcoming of promoting a dendritic type of metallic growth in the case of a solid (spongy structure) anode which contributes to cell failures by shortcircuiting to the cathode.

1. Effects of Inhibitors Under Static Conditions

One approach to the control of dendritic growth on a conventional zinc anode during the charging operation is to minimize or eliminate the electrodeposition process by eliminating zincate from the electrolyte and preventing its formation therein during cell operation. One pursuit toward this end was a search for inhibiting agents to be added to the electrolyte to achieve the effect of potassium zincate in minimizing chemical reactivity of the zinc with the electrolyte. Some of these inhibiting agents were found in the literature while others probably have never been investigated before. The static reactivity rates were determined by the amount of hydrogen gas liberated from 40% KOH by granulated zinc (99.9% purity) containing 13% mercury. Data are given in Table XI.

TABLE XI

Reactivity of Granulated Zinc Containing 13% Mercury
with 40% KOH Containing Various Inhibitors
as Measured by Hydrogen Gas Evolution

<u>Material</u>	<u>% by wt</u>	<u>ml electrolyte per gram metal</u>	<u>ml gas per gram metal</u>	<u>Temp</u>	<u>Time Hours</u>
Potassium Sulfide	23.27	10	1.4	Ambient	960
Potassium Chromate	1.0	10	2.0	Ambient	264
Lithium Chromate	2.0	10	0.1	Ambient	1200
Sodium Silicate	0.5	10	0.1	Ambient	1200
Potassium Selenite	0.9	10	None	Ambient	1200
Chromium Gluconate	2.5	10	0.4	Ambient	1056
Potassium Tellurite	0.7	10	0.1	Ambient	888
Potassium Stannate	0.5	10	0.4	Ambient	888
Lithium Chromate	2.0	3.7	1.0	160°F	168
Potassium Selenite	0.9	3.7	None	160°F	240
Potassium Zincate	13.4	3.7	.22	160°F	24
Potassium Zincate	13.4	3.7	.22	160°F	216

2. Effects of Inhibitors Under Dynamic Conditions

A series of charge and discharge tests were conducted in the exploratory research cell to assess the effect of selenium dissolved in the electrolyte on cell operation. In one series 40% KOH electrolyte containing 0.9% potassium selenite (introduced as SeO_2) was used while in another series 40% KOH-6.25% ZnO electrolyte containing also 0.9% potassium selenite was used. In general discharge utilization was lower when the electrolyte contained selenium without zinc oxide, high charging voltages were encountered when attempts were made to recharge the capacity equivalent to the discharge capacity. (High charging voltages were also encountered in the research cell near the end of charge when electrolyte without zinc oxide was used.)

While potassium selenite is highly effective in eliminating gas evolution during static tests, it does not prevent reactivity between zinc and KOH. Both zincate and elemental selenium were found in the electrolyte by chemical analysis. This would indicate that eventually all the selenium in the electrolyte would be liberated from the solution as elemental selenium (which was observed) with an equivalent amount of zinc dissolved.

Although the amount of gas produced in the sulfide containing electrolyte was rather high, in the interest of preventing the anodic dissolution of zinc to potassium zincate in favor of promoting the formation of solid and insoluble anode corrosion products, charge and discharge experiments were conducted with an electrolyte containing potassium sulfide. The object in preventing the dissolution of zinc is to preclude the electrodeposition process of the metal during the charging operation. In employing potassium sulfide (K_2S) electrolyte the anode corrosion product would be zinc sulfide (ZnS), a compound which is highly insoluble in alkaline solutions.

The electrolyte was prepared by introducing hydrogen sulfide gas (H_2S) into a solution of 40% KOH to the extent that a substantial amount was converted to the sulfide. The resulting solution contained 20.4% K_2S based on sulfur content. In evaluating this electrolyte as to discharge capability in the research cell with an anode amalgam of 5% zinc, it was found that the anode polarized within a few seconds when a discharge rate of 300 ma/in² was attempted. Apparently, due to the highly insoluble nature of the anode corrosion product, ZnS , an insulating film of the material immediately stopped further anode activity. This would lend support to the concept that to achieve high anode rates the zinc dissolution process should prevail.

The sulfide electrolyte was also evaluated with both reduced zinc oxide (sponge zinc) and amalgamated zinc powder type electrodes in addition to the 95% Hg-5% Zn anode described above. Very low efficiency was obtained on discharge, even at low current densities, and recharging could not be accomplished within the normal voltage range. Also when attempts were made to discharge zinc anodes with a silver terminal contact considerable gas evolution was experienced. This gassing was apparently due to a galvanic couple between zinc and silver. It is well known that the material (silver) contacting the zinc electrode in cells with alkaline electrolyte must be covered with zinc and that this process is usually accomplished by having zinc ions in the electrolyte (potassium zincate) as the source of zinc for galvanic deposition. Since zinc ions cannot exist in electrolyte containing sulfide ions (zinc sulfide precipitates), the silver does not become coated with zinc and a gassing couple between zinc and silver exists.

C. Separator Study

The alkaline-zinc secondary cells represent the most difficult systems to achieve effective long life electrode separation. In these systems the separator material must have a high resistance

to the chemical effects of the strong alkaline electrolyte, to the depolarizer and certain metal ions in solution, and it must be resistant to the physical effects of the electrodes especially the dendritic growth from the conventional solid zinc anode. Considerable effort has been expended in recent years in many laboratories to improve separators for the alkaline-zinc systems and this has led to the use of some form of ion-permeable membrane. There are only a few materials that are sufficiently low in electrical resistance and have sufficiently small pore size to prevent zinc crystal growth. Regenerated cellulose is by far the most commonly used. Because of the chemical degradation of cellulose in strong oxidizing alkaline media, a second separator is usually employed adjacent to the depolarizer material. The pore size of this member can be somewhat larger, but it should be capable of trapping colloidal particles.

One important part of a separator study is the means used to measure the degree of degradation. Most of the methods reported in the literature are concerned with determining the metal content of the membrane resulting from its reaction with certain metallic constituents of the cell elements. Other examinations are by visual means. As described in the Methods and Instrumentation section, the three methods of measurement used during this work were: (1) tensile strength, (2) electrical resistance, and (3) chemical analysis for metal content.

The separator materials reported here are identified by abbreviation mainly to denote the chemical composition. Following the chemical abbreviations certain code numbers and letters will further describe the material. The following table identifies the various materials by chemical name and abbreviation:

<u>Chemical Composition</u>	<u>Abbreviation</u>
Regenerated cellulose	C
Polyvinylchloride	PVC
Polyvinylchloride-acrylonitrile copolymer	PVC-A
Polyethylene	PE
Polypropylene	PP
Polytetrafluoroethylene	TFE

Most effort has been concentrated on an evaluation of those materials which are now commercially available, however, some data are presented for modified and specially prepared materials.

1. Effects of Electrolyte on Separator Materials Under Static Conditions

In assessing the effect on the electrolyte on the various materials, an elevated temperature was employed in most cases in order to hasten the degradative processes. Also, since 160°F is the upper limit of the temperature requirement of the contract, this value was chosen for most tests. To conduct investigations at this temperature require they be done in tightly sealed containers

to prevent evaporation of water from the electrolyte and absorption of oxygen and carbon dioxide from the air.

Specimens measuring 2.156" in diameter of the various materials, along with the 40% KOH-6.25% ZnO electrolyte solution were placed in the tightly sealed containers. The electrical resistance and tensile strength measurements were made initially and then after the exposure periods indicated. These data are presented in Table XII.

TABLE XII

Room Temperature Electrical Resistance and Tensile Strength of Separator Materials after Exposure to 40% KOH-6.25% ZnO Electrolyte

Separator (Dry thickness)	Exposure Time & Temp.(°F)	Resistance(Milliohms-in ²)				Tensile Strength (lbs/in ²)
		Sample #1	Sample #2	Sample #3	Aver.	
C-1 0.004"	3 hrs. @ 70	72	80	72	75	2440
	3 days @160	85	83	75	81	2603
	14 days @160	88	90	88	88	2140
	28 days @160	80	63	75	73	----
	21 days @ 70	48	50	40	46	1990
C-2 0.004"	3 hrs. @ 70	55	58	55	56	7710
	3 days @160	60	60	60	60	----
	14 days @160	83	80	80	81	3720
	28 days @160	63	58	68	63	----
	21 days @ 70	50	30	38	39	3810
C-3 Lot #1 0.0015"	3 hrs. @ 70	61	81	118	87	2540
	3 days @160	80	85	85	83	----
	14 days @160	75	40	63	59	2392
	28 days @160	53	53	53	53	196
	21 days @ 70	225	200	205	215	----
C-3 Lot #2 0.002"	3 hrs. @ 70	363	450	243	352	3040
	3 days @160	125	125	100	117	3095
	14 days @160	63	70	70	68	1600
	28 days @160	88	68	75	77	----
	21 days @ 70	--	--	--	--	----
C-3 Lot #3 0.0015"	3 hrs. @ 70	--	--	--	--	----
	3 days @160	63	63	40	54	2520
	14 days @160	55	63	50	56	3090
	28 days @160	--	--	--	--	----
	21 days @ 70	--	--	--	--	----
C-3 Lot #4 0.0015"	3 hrs. @ 70	--	--	--	--	----
	3 days @160	338	475	113	309	4800
	14 days @160	225	300	95	207	5290

TABLE XII (continued)

Separator (Dry thickness)	Exposure Time & Temp. (°F)	Resistance (Milliohms-in ²)				Tensile Strength (lbs/in ²)
		Sample #1	Sample #2	Sample #3	Aver.	
	28 days @160	--	--	--	--	----
	21 days @ 70	--	--	--	--	----
C-3	3 hrs. @ 70	--	--	--	--	----
Lot #5	3 days @160	565	425	400	463	7320
0.002"	14 days @160	420	300	218	313	8540
	28 days @160	--	--	--	--	----
	21 days @ 70	--	--	--	--	----
PVC-1	3 hrs. @ 70	10	10	--	10	580
	3 days @160	63	65	65	64	----
0.010"	14 days @160	75	75	75	75	500
	28 days @160	--	--	--	--	399
	21 days @ 70	38	38	38	38	----
PVC-2	3 hrs. @ 70	15	20	--	17	387
	3 days @160	60	83	55	66	----
0.010"	14 days @160	48	38	38	41	205
	28 days @160	--	--	--	--	290
	21 days @ 70	25	25	25	25	----
PVC-A-1	3 hrs. @ 70	55	65	90	70	4760
	3 days @160	20	20	20	20	6823
0.005"	14 days @160	55	58	55	56	6730
	28 days @160	20	15	15	15	----
	21 days @ 70	23	25	13	20	4800
PVC-A-2	3 hrs. @ 70	12	20	20	17	4370
	3 days @160	28	28	28	28	----
0.005"	14 days @160	45	43	38	42	3418
	28 days @160	0	13	15	9	3686
	21 days @ 70	30	35	33	33	----
PE-1	3 hrs. @ 70	113	122	122	119	3790
	3 days @160	98	95	85	93	----
0.001"	14 days @160	113	90	113	105	2392
	28 days @160	95	95	113	101	3091
	21 days @ 70	75	130	95	100	----
PE-2	3 hrs. @ 70	263	--	--	263	326
	3 days @160	130	125	163	139	----
0.010"	14 days @160	175	175	238	196	277
	28 days @160	--	--	--	--	350
	21 days @ 70	170	295	195	220	----

TABLE XII (continued)

Separator (Dry thickness)	Exposure Time & Temp. (°F)	Resistance (Milliohms-in ²)				Tensile Strength (lbs/in ²)
		Sample #1	Sample #2	Sample #3	Aver.	
PE-3 0.010"	3 hrs. @ 70			More than 50 ohms	157	
	3 days @160	165	153	(788)	159	----
	14 days @160	110	105	(513)	108	153
	28 days @160	--	--	--	--	85
	21 days @ 70	3300	3375	5250	3975	----
PE-4 0.005"	3 hrs. @ 70	950	950	--	950	338
	3 days @160	103	138	280	174	----
	14 days @160	55	88	200	114	334
	28 days @160	--	--	--	--	116
	21 days @ 70	978	4028	6903	3969	----
PP-1 0.001"	3 hrs. @ 70	140	150	110	133	2550
	3 days @160	108	85	73	89	3680
	14 days @160	85	95	83	87	5206
	28 days @160	70	43	50	54	----
	21 days @ 70	100	80	65	82	----
TFE-1 0.0015"	3 hrs. @ 70	53	75	53	60	3240
	3 days @160	1025	1025	1020	1023	2510
	14 days @160	1123	963	943	1010	2410
	28 days @160	1120	1163	1113	1150	----
	21 days @ 70	120	95	150	122	----

*() values not included in average

Interpretation of the tensile strength measurements of the PVC-A materials is difficult due to the presence of a reinforcing base material. Also the strength of the microporous plastics is somewhat dependent upon orientation of the polymeric chains. Tensile values will vary depending on the grain or extrusion direction.

During these studies, it was found that many of the membrane type separators exhibited poor wettability in 40% KOH-6.25% ZnO electrolyte, but were readily wetted by 40% (or lower) concentrations of KOH, or by water. Some of the membranes required more than 3 hours exposure to the ZnO containing electrolyte to reach minimum resistance.

2. Stability of Separators in Completed Cells Under Static Conditions

In addition to the static electrolyte resistance tests, a version of Test Vehicle #2 (see Experimental Fabrication and Cycle

Testing section) has been used to study the stability of separators when positioned near or adjacent to their appropriate electrodes during static conditions. The positive electrode was prepared by charging the 69% Hg-31% Ag alloy. The negative electrode employed was amalgamated zinc in granular form. A non-woven absorbent-separator 0.004" thick was placed between the positive electrode and the positive barrier-separator in all cells. A 1/8" mesh woven polyethylene screen was placed between the positive and negative separators to insure separation of the two members. The resistance, metal content and tensile strength data are presented in Table XIII.

TABLE XIII

Characteristics of Separators Exposed to
Cell Electrodes Under Static Conditions

Cell No.	Separator		Exposure Test(Days at 160°F)	Resistance (Milliohms-in ²)	Metal Content (Milligrams/in ²)		Tensile Strength (lbs/in ²)
	Positive(+)	Negative(-)			Hg	Ag	
45	PVC-1	(+)	28	20	2.3	0.86	----
	C-2	(-)		55	11.6	0.2	----
46	PVC-1	(+)	28	20	3.8	0.7	----
	C-2	(-)		43	7.0	nil	----
47	PVC-1	(+)	28	30	10.5	0.76	----
	C-2	(-)		55	8.6	nil	----
59	PP-1	(+)	14	75	---	---	1100
	C-1	(-)		80	---	---	518
60	PP-1	(+)	14	--	3.12	3.15	----
	C-1	(-)		--	6.15	0.25	----
63	PP-1	(+)	14	200	---	---	9880
	C-1	(-)		20	---	---	----
61	PP-1	(+)	31	125	---	---	6350
	C-1	(-)		105	---	---	305
62	PP-1	(+)	31	--	15.63	nil	----
	C-1	(-)		--	7.51	0.54	----
70	TFE-1	(+)	20	198	---	---	2060
	C-3	(-)		60	---	---	1460
71	TFE-1	(+)	20	208	---	---	2490
	C-3	(-)		45	---	---	768

TABLE XIII (continued)

Cell No.	Separator		Exposure Test(Days at 160°F)	Resistance (Milliohms-in ²)	Metal Content (Milligrams/in ²)		Tensile Strength (lbs/in ²)
	Positive(+)	Negative(-)			Hg	Ag	
72	TFE-1	(+)	20	--	4.2	1.3	----
	C-3	(-)		--	1.9	3.1	----
73	TFE-1	(+)	31	280	---	---	2200
	C-3	(-)		63	---	---	1830
74	TFE-1	(+)	31	198	---	---	2120
	C-3	(-)		68	---	---	610
75	TFE-1	(+)	31	--	4.65	4.26	----
	C-3	(-)		--	7.67	nil	----
82	PE-1	(+)	14	113	---	---	2020
	C-3, Lot #3	(-)		48	---	---	650
83	PE-1	(+)	14	80	---	---	5070
	C-3, Lot #3	(-)		38	---	---	650
84	PE-1	(+)	28	113	---	---	2000
	C-3, Lot #3	(-)		38	---	---	244
85	PE-1	(+)	28	88	---	---	2000
	C-3, Lot #3	(-)		50	---	---	894
86	PE-1	(+)	14	--	0.63	nil	----
	C-3, Lot #3	(-)		--	6.72	nil	----
87	PE-1	(+)	28	--	5.25	3.60	----
	C-3, Lot #3	(-)		--	22.50	0.48	----
88	PVC-A-1	(+)	14	28	---	---	----
	C-1	(-)		70	---	---	368
89	PVC-A-1	(+)	14	30	---	---	----
	C-1M	(-)		138	---	---	706
90	PVC-A-1	(+)	14	35	---	---	----
	C-2	(-)		105	---	---	1770
91	PVC-A-1	(+)	14	30	---	---	----
	C-2M	(-)		155	---	---	2980

Due to small sampling only trends are represented by these data, however, the PVC-1 appears to have excellent electrical resistance stability and the PP-1 has outstanding tensile strength.

3. Stability of Separators in Cells Under Dynamic Cycle Conditions

The characteristics of some of the separators removed from Test Vehicle #2 type cells which were cycle tested on a 2 hour simulated satellite orbit have been studied. A generalized separator system from the surface of the positive electrode toward the negative electrode is as follows: 0.004" non-woven absorbent-separator, positive electrode barrier-separator, cellulosic absorbent-separator, negative electrode barrier-separator. In some cases two layers of each electrode separator were used. The resistance and metal content data obtained are given in Table XIV.

TABLE XIV

Characteristics of Separators Exposed to
Cycle Conditions in Test Vehicle #2

Cell No.	Separator	Cycles	Resistance (Milliohms-in ²)	Metal Content (Milligrams/in ²)	
	Positive (+) Negative (-)			Hg	Ag
432	PVC-A-1 (+)	770	33	--	--
	Cellulose				
	Absorbent		--	6.8	9.6
	C-1 (-)		88	--	--
442	PVC-A-1 (+)	790	50	--	--
	C-1 (-)		93	--	--
441	PE-1 (+1)	910	63	3.3	14.6
	PE-1 (+2)		50	0.9	0.7
	Cellulose				
	Absorbent		--	4.8	0.3
	C-3 (-2)		88	1.3	nil
	C-3 (-1)		45	0.05	nil
451	PVA-A-1 (+)	670	30	--	--
	Cellulose				
	Absorbent		--	12.5	10.5
	C-1 (-)		130	29.7	1.3
443	PVA-A-1 (+)	700	30	--	--
	C-1 (-)		93	--	--
440	PE-1 (+1)	780	63	2.6	10.2
	PE-1 (+2)		30	1.3	nil
	Cellulose Absorbent		--	2.5	nil
	C-3 (-2)		125	1.9	nil
	C-3 (-1)		55	1.3	nil

While not conclusive these data indicate that two layers of PE-1 material maintains silver and mercury migration at a low level in the 700 cycle range.

4. Modified Separator Materials

Through the co-operation of a material supplier, samples of C-1 and C-2 cellulosic membrane materials were modified by a proprietary process to increase resistance to chemical degradation and to increase tensile strength. Electrical resistance and tensile strength measurements were made initially and after exposure in 40% KOH-6.25% ZnO electrolytes at 160°F of both the modified and unmodified materials. Data are given in Table XV.

TABLE XV

Room Temperature Electrical Resistance and
Tensile Strength of Regular and Modified C-1 & C-2
Separator Materials after Exposure to Electrolytes

Separator (0.004" dry thickness)	<u>Exposure</u>		<u>40% KOH</u>		<u>40% KOH-6.25% ZnO</u>	
	Time (Days)	Temp (°F)	Resistance (Milliohm-in ²)	Tensile Strength (lbs/in ²)	Resistance (Milliohm-in ²)	Tensile Strength (lbs/in ²)
C-1	1	70	39	2389	69	3560
	3	160	46	1100	75	1620
	14	160	50	1320	67	1890
	28	160	50	1920	67	2040
C-1M	1	70	57	3520	76	5210
	3	160	57	3810	89	2560
	14	160	57	3460	77	3960
	28	160	57	3990	77	5090
C-2	1	70	30	4980	53	4760
	3	160	34	4230	43	3960
	14	160	35	4940	51	5480
	28	160	43	4730	52	4820
C-2M	1	70	60	5750	93	6000
	3	160	53	5300	88	5060
	14	160	56	7370	82	5360
	28	160	52	5730	78	5640

The modified materials are higher in both electrical resistance and tensile strength. In particular, a significant increase in tensile strength of C-1 material was obtained. Resistance values measured in ZnO type electrolyte are as much as 50% higher than those measured in KOH electrolyte without ZnO. The resistance remained quite constant over the test period in this environment.

In addition to the commercially available materials which were modified another approach toward obtaining improved separators was initiated. Small samples of regenerated cellulose reinforced with alkali resistant materials were prepared. These materials were non-woven fabrics, commercially available. The electrical resistance of the initial samples was 20 to 50 milliohms-in². While only cursory information is available from these tests, the principle of reinforcing regenerated cellulose with alkali resistant material does appear to have merit.

D. Positive Electrode Study

Since mercuric oxide is essentially a non-conductor and its reduction product is a liquid, some other material must be used with it to maintain a solid conductive matrix. From previous experience it is strongly indicated that from most standpoints silver powder of very small particle size is the best material. When amalgamated and compacted into the desired shape, this material produces a rigid porous electrode having a high electrical conductivity and affording a reservoir for mercury.

According to the mercury-silver constitution diagram, the lowest amount of silver that will form a solid alloy at room temperature with mercury is 29%. Alloys containing 29% to 30.5% silver are gamma phase which have a strong tendency to develop metastable conditions during cooling. As a consequence, most effort has been with the alloy 69% mercury-31% silver. This alloy is beta plus gamma phase and is composed of both close-packed hexagonal and body-centered cubic crystals.

The initial phase of the positive electrode study was a thorough evaluation of its charge and discharge characteristics in its present state of development with respect to the technical requirements of the project. With a charge-discharge cycle equivalent to a low altitude orbit, it can be established that the optimum charge acceptance current density of the positive electrode will dictate the electrode area needed to meet the required power output. If, for instance, a 300 ma/in² discharge rate is chosen for a 2 hour orbit (35 minutes discharge, 85 minutes charge) both electrodes must be capable of accepting charge at 123.5 ma/in². For comparison purposes, the recommended charging rate for the Ag-Ag₂O electrode is sometimes as low as 25 ma/in² for a long efficient cycle life.

The exploratory research cell, having 0.235 in² electrode area and 0.25" electrode spacing, was used for evaluations. For initial tests the electrode contact consisted of a 0.010" thick silver disc with a silver lead wire welded to one side and an expanded silver screen welded to the other side. The active material, weighing 0.44 grams (equivalent to 82 ma-hrs of HgO), was pressed onto the side with the expanded screen producing an electrode with an overall thickness of approximately 0.032". In order to make the depolarizer the rate limiting member, an

excess of electrolyte and an excess of negative electrode material was used for these investigations. The charging rate of 128 ma/in² was chosen because it corresponds closely to a 300 ma/in² discharge rate for a simulated 2 hour orbit. Data are presented in Table XVI and graphically in Figure 11.

TABLE XVI

Consecutive Discharges of a Ag-HgO Electrode After
a Charge Cycle of 85 minutes at 128 ma/in²

<u>Charge Rate (ma/in²)</u>	<u>Theoretical Charged Capacity (ma-hrs)</u>	<u>Discharge Rate (ma/in²)</u>	<u>Discharge Capacity (ma-hrs)</u>	<u>Utilization (%)</u>
128	42.5	600	42.3	99.5
128	42.5	800	41.4	97.3
128	42.5	1000	42.1	99.0
128	42.5	1200	40.0	94.0
128	42.5	1400	42.0	98.9

In the interest of increasing the charging rate above that reported in Table XVI, a preliminary experiment was conducted at 247 ma/in² of electrode area. This charging rate is equivalent to a 600 ma/in² discharge rate for a 2 hour cycle. Some loss in charge efficiency was experienced as indicated by the curves given in Figure 12.

Further charge and discharge experiments conducted with the research cell invariably gave rise to a serious physical distortion of the positive electrode. The electrode assumed a shape which was concave with respect to the anode. Toward minimizing or eliminating this undesirable behavior and also toward increasing the charge acceptance rate, experiments were conducted in which palladium was incorporated in the electrode matrix. This was first accomplished by electroplating the silver powder with palladium using a commercial plating solution. As an example, in one experiment 0.95% palladium metal was applied to the silver particles to result in a 0.30% Pd content in the final electrode after the 70% mercury was added.

Prior to rate determinations the palladium-containing electrodes were studied from the standpoint of electrode potential during the charging operation. The presence of palladium effects a lower electrode potential throughout the charging operation with no evidence of the formation of Ag₂O prior to gas evolution as measured by X-ray diffraction. At the end of charge the potential suddenly rises to the value of 2.1 volts (total cell voltage) with evolution of oxygen gas. Conversions of mercury to HgO and silver to Ag₂O to the extent of 80%-87% of theoretical at a charge rate of 128 ma/in² were obtained. The effect of palladium in the positive electrode during charging is shown in Figure 13.

During further evaluation of positive electrodes, the palladium was applied by chemical displacement from a palladium salt solution. Also depolarizer material was coated after the amalgamation process by both the electrodeposition method and the chemical displacement method. Better results were obtained when the silver powder was coated with palladium (by either method) prior to the amalgamation process.

The charge acceptance was studied in the exploratory research cell under uninhibited conditions (i.e., excess electrolyte and no separators). The 0.010" thick silver disc was omitted to make the electrode contact a silver lead wire welded to an expanded silver screen. The active material was pressed into the expanded screen. Cycle regime usually consisted of the following: two complete cycles of 123.5 ma/in² constant current charge to near gassing potential (approximately 0.6V vs HgO-Hg-Ag reference electrode) and constant current discharge at 300 ma/in² to the onset of polarization. In all cases this discharge rate was employed. The charging rate was then increased by increments to 494 ma/in² (equivalent to a discharge rate of 1200 ma/in² corresponding to a two hour satellite orbit.) Charge rate was then decreased to 123.5 ma/in² or 247 ma/in² in order to study the effects of charging current density variation on charge acceptance. The theoretical capacity was based on Hg conversion to HgO and Ag to Ag₂O.

While the addition of palladium produced higher charge acceptance efficiencies, it did not minimize the electrode shrinkage and the accompanying decrease in charge acceptance encountered during cycling. Additive studies were initiated in an effort to overcome this condition. Positive electrodes containing separately each of the following additives: activated charcoal, activated charcoal containing 10% Pd, wood charcoal, graphite and polyethylene oxide have been cycled in the exploratory research cell as described above. Percentages of 0.5% to 3.0% were investigated. Also reduced particle size (i.e. minus 200 mesh, while prior to this minus 100 mesh had been employed) depolarizer material was investigated with respect to charge acceptance and densification. Some of the data obtained during these positive electrode studies are shown in Figure 14 through Figure 22.

The lower charge acceptance of electrodes without palladium on the depolarizer material is shown in Figure 17 and Figure 18 when compared to results shown in Figure 14 or Figure 19.

The downward trend in charge acceptance prevails in most of the Figures. Data in Figure 15, which were obtained with a charge rate of 123.5 ma/in², indicate the downward trend to be somewhat diminished when the higher charging rates were not imposed. All data seem to indicate a relationship between electrode efficiency and declining charge acceptance which in turn is related to electrode densification. Figure 16 and Figure 20 are examples. Figure 16 clearly shows the decrease in charge acceptance following efficient initial cycles and the accompanying densification is shown in the photograph. Figure 20 shows no decrease in charge acceptance and no physical change, but a much lower initial electrode efficiency.

While all of the previously described positive electrode investigations were designed to obtain maximum electrode efficiency without due regard to voltage, it is now quite apparent that a battery composed of cells discharging at the Zn-Ag₂O voltage level and then the Zn-HgO voltage level during the same cycle will not remain within the contract voltage requirement of 27.5 ± 1.5 volts. To meet this requirement the individual cells in a 22 cell battery would have to operate between 1.318 volts and 1.18 volts and in a 23 cell battery they would have to operate between 1.26 volts and 1.13 volts.

Since the optimum charge acceptance current density of the positive electrode will apparently dictate the electrode area needed to produce the required output, additional charge acceptance evaluations at lower voltages have been initiated. The maximum allowable charging voltage has been established at 1.48 to 1.50 volts. Electrode area and thickness must be optimized for the power requirement.

E. Experimental Fabrication and Cycle Testing

Further evaluation by extended cycle testing of promising electrode-electrolyte systems resulting from the research phases necessitated some version of a test cell. This enabled the determination of and improvement in the various cell parameters such as charge and discharge rate capability, electrode spacing, separator system, percent utilization per cycle, and other factors. The early effort dealt with the design, evaluation and use of two experimental charge and discharge test vehicles.

1. Test Vehicle #1

Initially a rectangular plastic cell was evaluated. The plastic case, constructed of "Plexiglass" accommodated electrodes 1-1/2" x 2" in size. Provisions could be made to measure the volume of gas generated by the displacement of water from a graduated tube. Also, the incorporation of a reference electrode made the design versatile in that the electrodes were studied under actual operating conditions.

The uncharged positive electrode for the plastic cell was prepared by compacting the 69%-31% mercury-silver alloy powder on an expanded silver screen having a welded silver lead. The electrode thickness was 0.031".

The uncharged negative electrode was prepared by applying a paste of zinc oxide and KOH to an expanded silver screen to make an electrode of approximately 0.015" thickness.

Absorbent cellulose paper, 0.008" thick was placed on each side of the anode for electrolyte absorption. A regenerated cellulose barrier and a microporous plastic barrier was employed. The useful electrode area was 6 in² with one negative and two positive plates.

Only a few of these cells were constructed. The discharge rate achieved was not encouraging. One cell with this electrode geometry gave as much as 1950 ma-hrs discharge capacity for 5 cycles. The discharge rate was 300 ma and the charge rate was 100 ma to 1.7 volts.

Cycling was continued at a 1 ampere discharge rate to 0.9V and a charge rate of 0.46 ampere to 1.9V. Output capacity during the first 10 cycles averaged 990 ma-hrs. Capacity then gradually decreased to 511 ma-hrs at the 38th cycle representing a loss of about 50% during the high rate cycling. The low efficiency obtained was attributed to poor contact between the electrode surfaces and the separators.

This structure was abandoned in favor of Test Vehicle #2.

2. Test Vehicle #2

The further evaluation and use of a second design test vehicle, Figure 23, was initiated. This is a sealed cell, 2-5/16" diameter x 1/4" height, having two electrode cups of the same diameter and each having an internal area of 3.14 in². The seal is made by crimping over a neoprene gasket.

The positive electrode cup is prepared by welding expanded steel screen to one of the steel cups and electroplating with silver. The mercury-silver alloy is then pressed into the cup. The negative electrode cup can be steel electroplated with silver or a steel cup with a thin sheet silver liner into which the anode paste is applied. Various separator materials have been employed and a more positive separation is assured by clamping the edge of same between the gasket and the flange of one electrode cup.

Considerable past experience has been accumulated with this structure. Experimental cells of this design made prior to this contract have yielded over 1000 cycles at room temperature on a simulated satellite schedule.

3. Cycle Testing of Individual Cells

Automatic cycle testing of experimental Test Vehicle #2, with individual cell control, was started when equipment became available. A two hour simulated satellite orbit of 35 minutes discharge, 85 minutes charge was used. The cells were discharged through a fixed resistance of 1.33 ohms which gave an average current drain of approximately 900 ma (about 300 ma/in² of electrode area) during the discharge period. During these tests no attempt was made to maintain the discharge voltage at the Zn-HgO level, consequently, a portion of discharge took place at the Zn-Ag₂O voltage level. The charging current employed was approximately 500 ma (not regulated) initial, tapering to a lower value as the limiting voltage was approached. For the electrode design and weight of active materials reported here this discharge represents 15% cycle depth based on the theoretical capacity of the depolarizer (Hg converted to HgO and Ag converted to Ag₂O).

The following three basic modifications were employed in the fabrication of these test cells. (1) Sheet silver liners were used in the anode cups instead of silver plated steel. (2) Palladium was added to the 69% Hg-31% Ag alloy positive electrode. (3) Various separator systems were employed. The anode used in all cells was a paste of ZnO and electrolyte thus making the cells in the discharged condition upon assembly.

Cycle life data are presented in Table XVII. In these data, high resistance means a closed circuit voltage below 0.9V. Also, only positive and negative separators are shown. In all cases a cellulose absorbent separator was employed between these members.

TABLE XVII

Automatic Cycle Testing of Test Vehicle #2

Cell No.	Separator Positive (+) Negative (-)	Modifications	Cycles	Status
29	PE-1 (+), C-1 (-)		1143	High Resistance
30	PVC-A-1(+), C-1 (-)		2398	Equipment Failure
31	" "		510	Internal Short
32	" "		770	High Resistance
33	" "		570	Internal Short
34	" "		450	Internal Short
35	" "		700	High Resistance
37	PE-1 (+), C-3 (-)		350	High Resistance
38	" "		1448	High Resistance
39	2 ea. PE-1(+), C-3 (-)		250	High Resistance
40	" "		760	High Resistance
41	" "		900	High Resistance
42	PVC-A-1(+), C-1 (-)	Ag Liner in anode can	790	Internal Short
43	" "	" "	700	Internal Short
44	" "	" "	2180	On Test
48	" "	0.3% Pd in depolarizer	1361	Internal Short
49	" "	" "	762	Internal Short
50	" "	" "	1132	Internal Short
51	" "	" "	671	Internal Short
65	PE-1 (+), C-3 (-)		395	Equipment Failure
66	" "		1163	Internal Short
68	PVC-A-1(+), C-2 (-)	Ag Liner in anode can	750	High Resistance
69	" "	0.3% Pd in depolarizer	650	High Resistance

Although valuable electrode and separator information has been obtained from these tests, it is now evident that a better choice of separator materials can be made in light of these data and information resulting from the separator study.

4. Cycle Testing of Series Connected Cells

Voltage controlled charging of series connected cells was accomplished with a power supply which is capable of producing a charging mode of any chosen current (up to 1.5 amps) up to a pre-set voltage. When the pre-selected voltage is reached it remains constant while the current tapers.

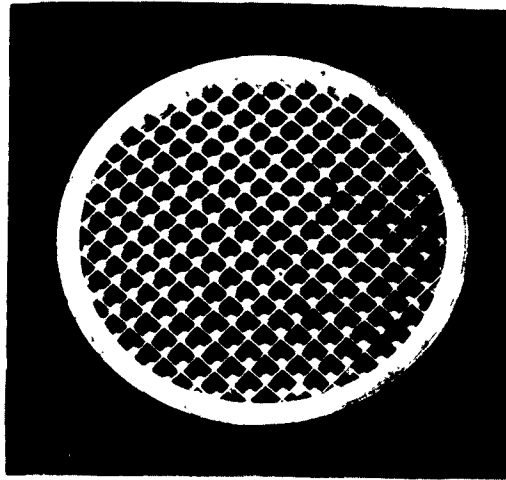
After an initial conditioning cycle, one battery of 10 series connected Test Vehicle #2 cells was fabricated and tested on the 35 minute discharge, 85 minute charge timed cycle. A fixed resistance of 12 ohms was employed for the discharge load. The regulated power supply was adjusted for 460 ma (145 ma/in^2 of electrode area) initial charging current and 17 volts maximum overall voltage.

The discharge voltage range was 14.1 volts to 11.1 volts for more than 70 cycles, but the end discharge voltage gradually decreased. After 89 cycles the end charging voltage on one cell was 1.77 volts while the remaining nine cells were 1.70 volts or less. In an effort to improve the discharge voltage the charging current was increased to 500 ma during cycle number 90. Cycling continued to 290 cycles. At this point the end of discharge voltage was 8.0 volts. The maximum charge voltage was then increased to 18 volts. On the 303rd cycle the first failure was experienced, i.e. voltage reversal during discharge and 2.3 volts during charge. After replacing the cell which failed, cycling was continued to 400 cycles. At this point the voltage at the end of discharge was 8.6 volts. The series string was disconnected and the cells were placed on individual cell control cycling. Sixty cycles were obtained, with the end discharge voltage above 1.0 volts, before the cells were reassembled in series and the cycling continued. The next failure, occurring on the 459th series cycle, was due to a shortcircuit. At 540 cycles the battery was disconnected and the cells again placed on individual cell control cycling. Approximately 80 more cycles have been completed to the present time.

From the information obtained during this first series cycle testing attempt, it is evident that the test vehicle employed is not capable of extended cycle life when operated at discharge rates in the range of 300 ma/in^2 and charge rates of 145 ma/in^2 . Better cycle life can be obtained at these rates during individual cell cycling, but the voltage excursion per cycle is not within the required battery voltage of 27 ± 1.5 volts.

5. Cells with Liquid Anode Retainers

Several Test Vehicle #2 cells were constructed with liquid anode retainers (as shown in photograph) containing a 90 Hg-10 Zn anode. The amalgam used contained enough zinc to discharge at 600 ma/in^2 for 35 minutes (based on the 2" diameter retainer). These cells have been discharged at 950 ma constant current (300 ma/in^2 of electrode area) to 0.9 volts and charged at 390 ma (123.5 ma/in^2 , corresponding to the 35 minute-85 minute discharge-charge relationship). Only a few cycles have been obtained but the discharge efficiency is in the range of 60% to 70% which compares favorably with the values obtained during the negative electrode evaluations in the research cell.



Photograph of Preliminary Specimen of
Liquid Anode Retainer for Test Vehicle #2

Toward obtaining a more constant voltage during discharge, i.e. absence of Ag_2O voltage, the charging voltage has been limited to 1.5 volts during cycle testing. Because of the lowered charge acceptance at this voltage the discharge current was also decreased. The discharge load is 4 ohms and the initial charging current is approximately 200 ma (not regulated), tapering to a lower value as the limiting voltage is approached. Under these conditions more than 150 cycles have been obtained with the discharge voltage range between 1.31 volts and 1.21 volts. Based on a 22 cell battery, this would represent 2.20 volts drop, which is within the 27 ± 1.5 volt requirement. Figure 24 contains two discharge curves for the same liquid anode cell comparing the discharge voltages obtained during cycle testing described in the previous two paragraphs.

6. Environmental Testing

In order to meet contractual requirements, the final battery design must be capable of withstanding an acceleration of 18 g and a shock of 40 g. Although a final design has not yet been established, preliminary acceleration and shock tests have been made on the liquid anode retainer. In these tests the retainer for the exploratory research cell was used.

A liquid anode of 90Hg-10Zn contained in the retainer was centrifuged at 18 g acceleration in three planes. This was done without the use of barriers or separators to retain the amalgam. The amount of amalgam used was the theoretical quantity necessary to sustain a 600 ma/in² discharge rate for 35 minutes. In these initial acceleration

tests, 12% of the anode material was lost in the plane where the compartment openings were pointing away from the centrifuge axis. No losses were experienced in the other two planes. In the preliminary shock tests 3% of the amalgam was lost when the force was applied perpendicular to but away from the compartment openings. None was lost when the force was applied in the other planes.

IV. SUMMARY AND CONCLUSIONS

1. From the discharge data reported, it is apparent the high mercury-zinc anode will sustain a high rate with excellent utilization. The compatibility of Zn-Hg-Ag in electrolyte containing zincate was proven as indicated by low hydrogen gas evolution.

2. The electrolyte addition agents studied were detrimental to cell performance or offered no discernible advantage.

3. Considerable data were accumulated on the effects of cell elements on various separator materials such as changes in electrical resistance and tensile strength, but no recommendation can be made for a separator system at this time.

4. Palladium in the positive electrode definitely improves the charge acceptance characteristic of this electrode. Deep cycling to convert virtually all the mercury and part of the silver to their oxides contributes to electrode densification as evidenced by shrinking and cracking.

5. While valuable separator and electrode data were obtained during automatic cycle testing of cells with individual voltage control at discharge current densities of approximately 300 ma/in² of electrode area, the voltage requirement of ± 1.5 volts (per 27.5 volt battery) was not met. At a maximum charge voltage of 1.5 volts per cell (to avoid conversion of silver) and at a discharge rate of 100 ma/in² the discharge voltage requirement was met. Cycle testing of 10 series connected cells was demonstrated by 300 cycles before a failure occurred.

V. RECOMMENDATIONS

It is recommended that the applied research be continued to the construction and testing of cells which are capable of the required 20 ampere discharge rate, since cycle capability of the Zn/KOH/HgO-Ag system has been demonstrated. It is further recommended that additional effort be expended in the following areas toward improved cycle life and voltage regulation.

1. Positive Electrode

A more thorough evaluation of the charge acceptance characteristics below the silver oxide formation voltage is required. Further evaluations of Hg-Ag alloys containing palladium and a search for a matrix material other than silver should be conducted.

2. Negative Electrode

In view of the indicated lower rate capability of the positive electrode when maintaining the required discharge voltage, the high rate capability of the high mercury-zinc anode in the retaining member may not be necessary. This indicates a simpler structure should be developed from this electrode.

3. Separator Evaluation

The further evaluation of modified and specially prepared materials, and those commercially available, is required to select the proper material for the final cell design.

4. Cell Fabrication and Testing

An intensified study of cell fabrication techniques and accompanying cycle testing should be made to enable the fabrication of a practical battery structure.

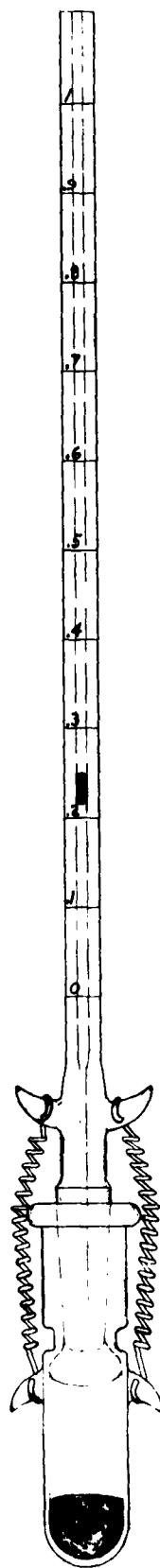


Figure 1 Reactivity Rate Apparatus-Method III

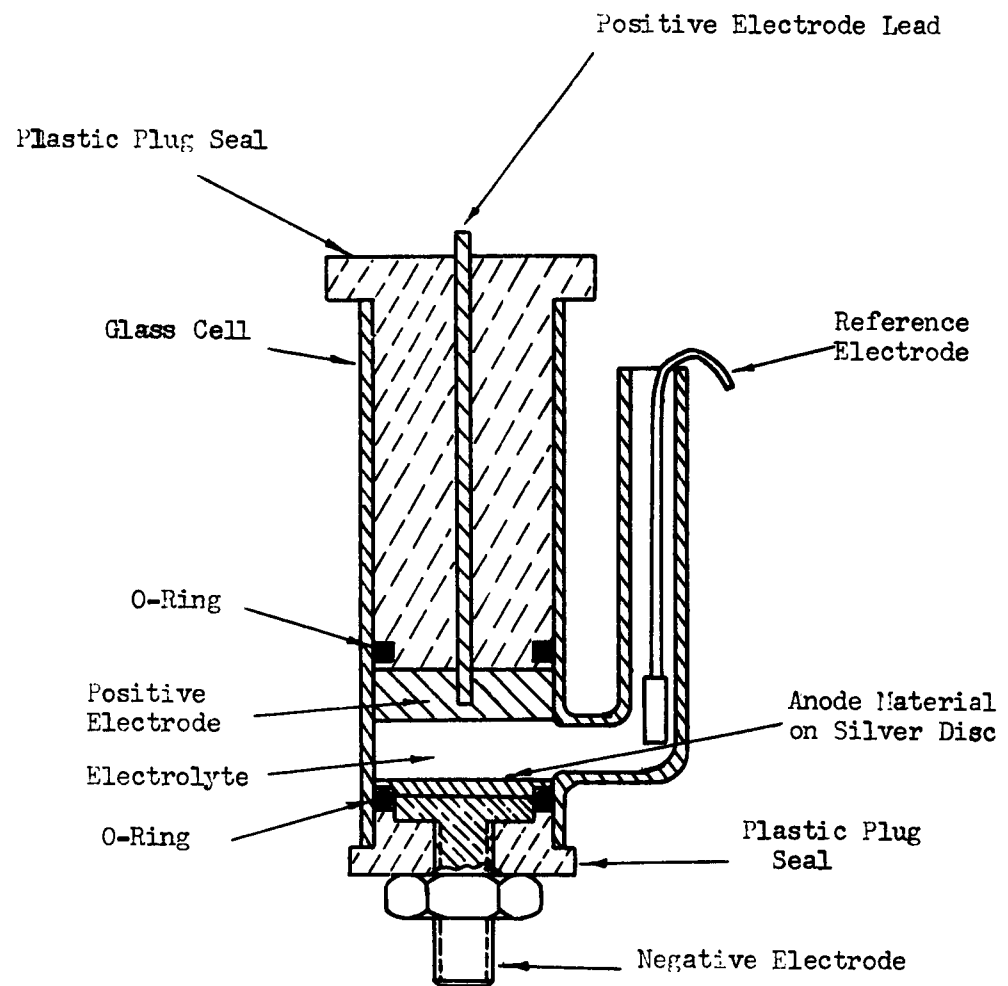


Figure 2 Glass Research Cell

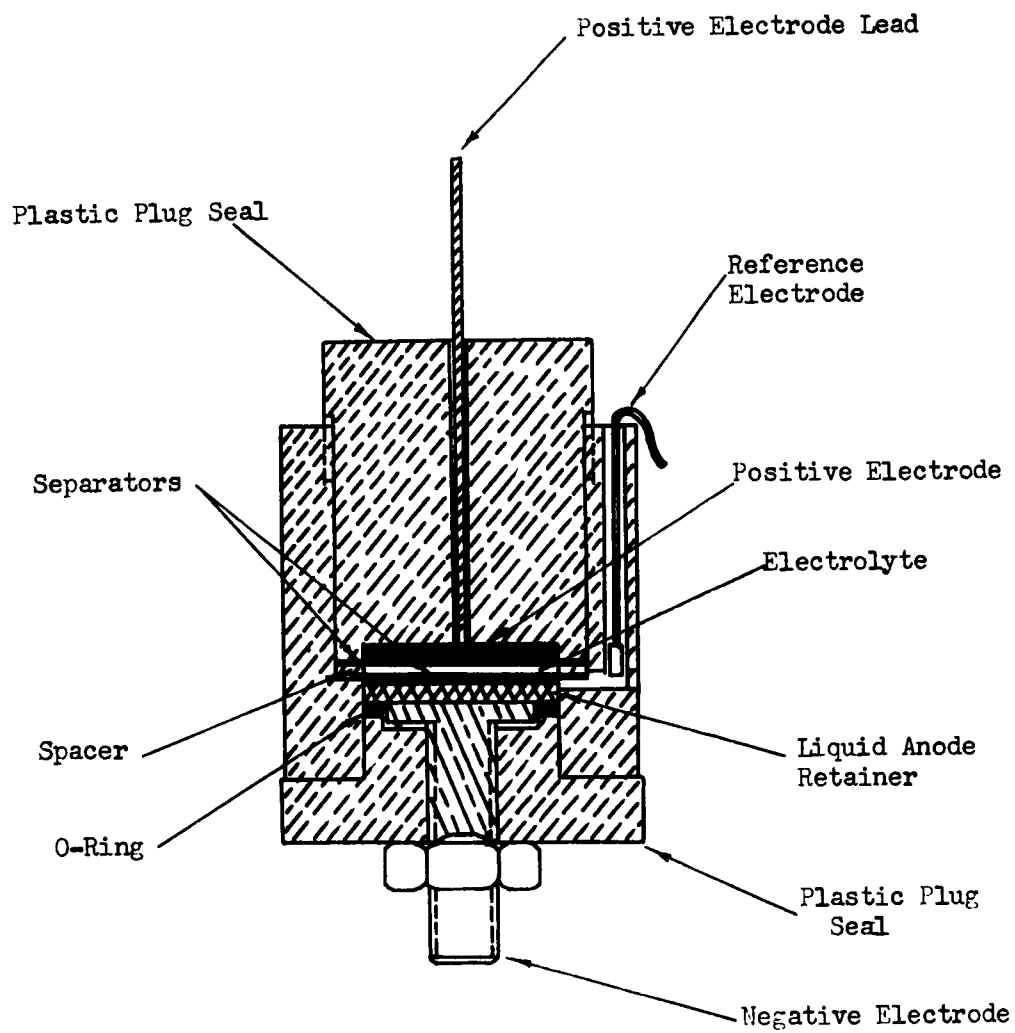


Figure 3 Plastic Research Cell

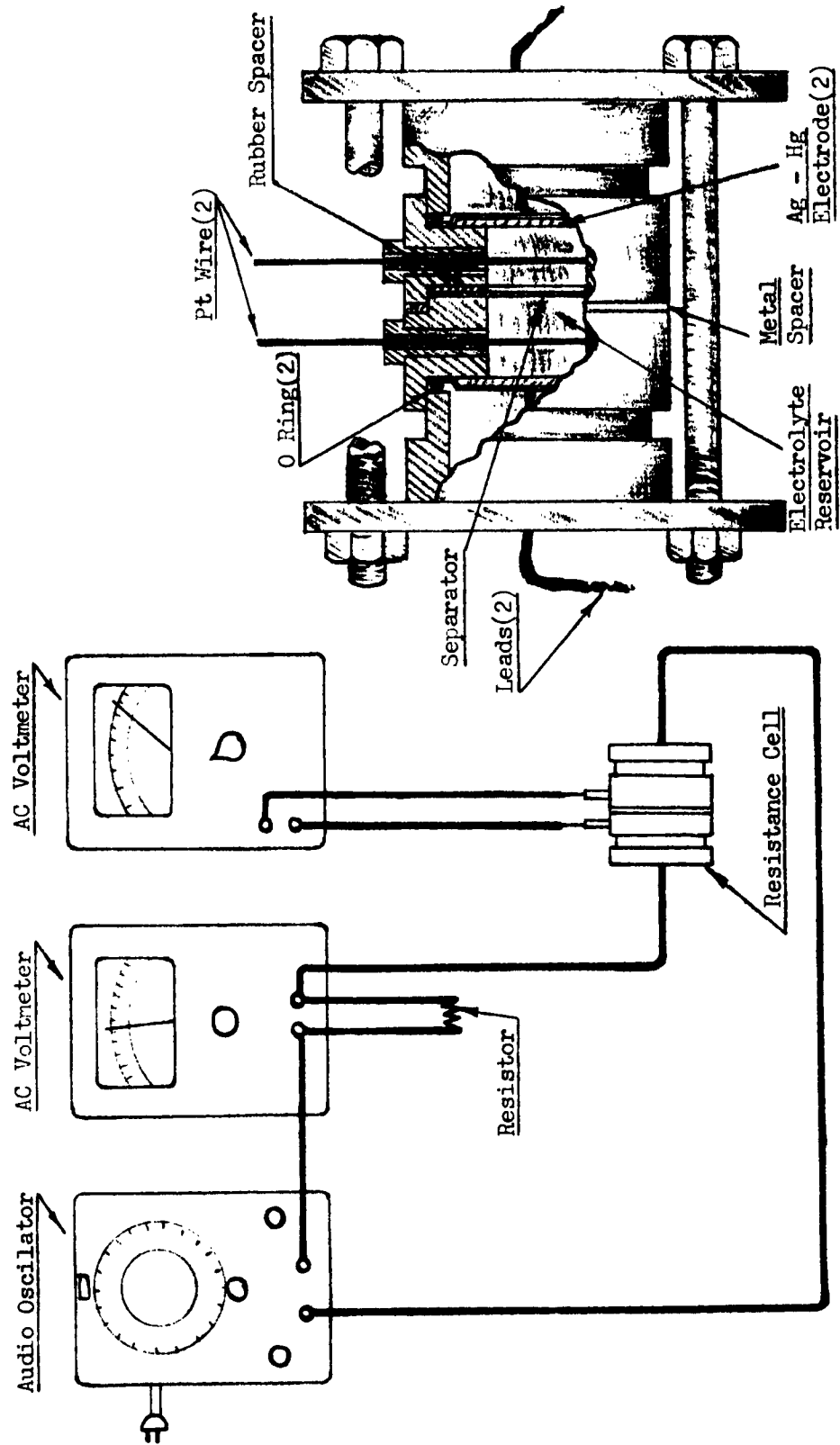


Figure 4 Determination of Separator Resistance

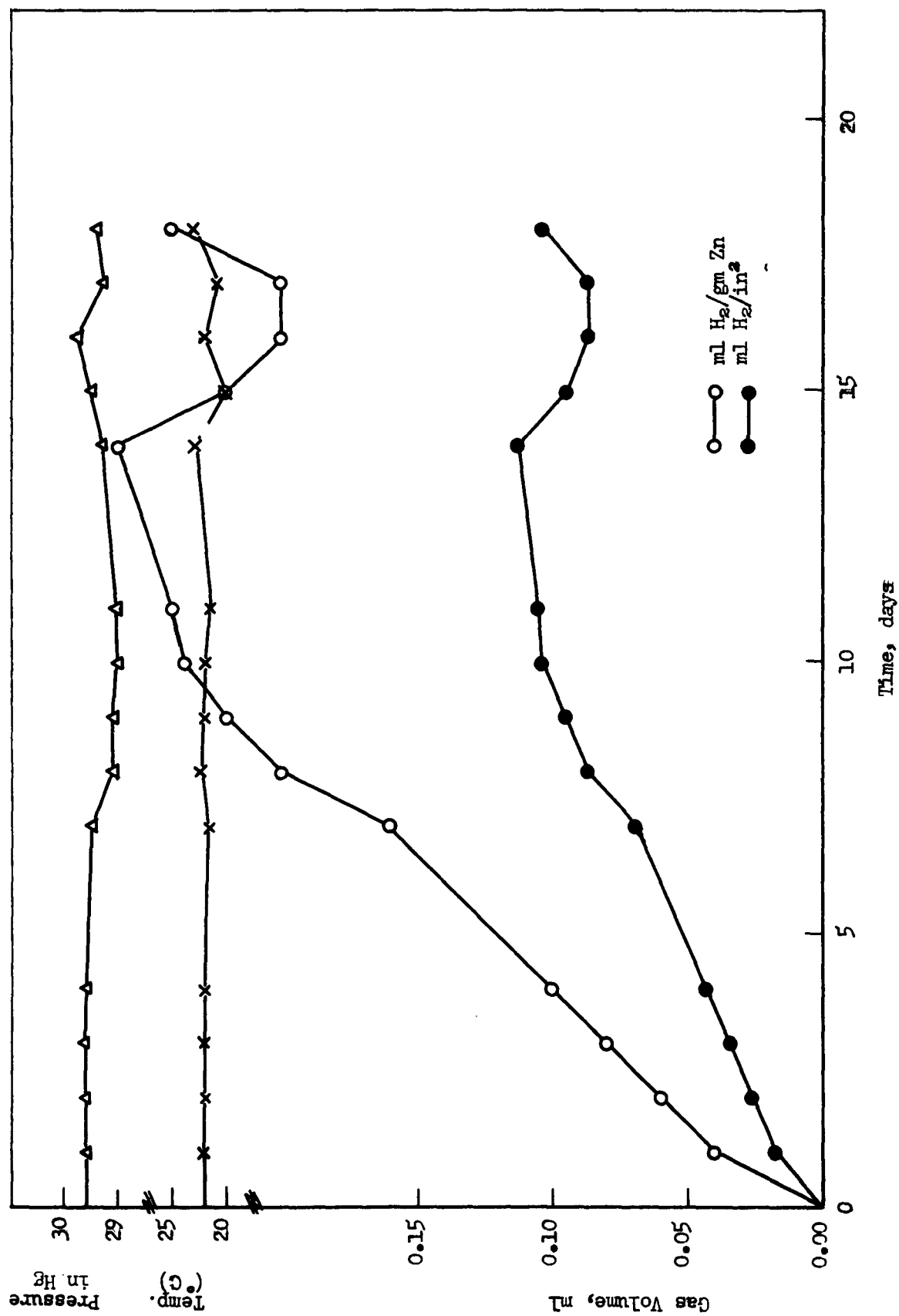


Figure 5 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH Electrolyte

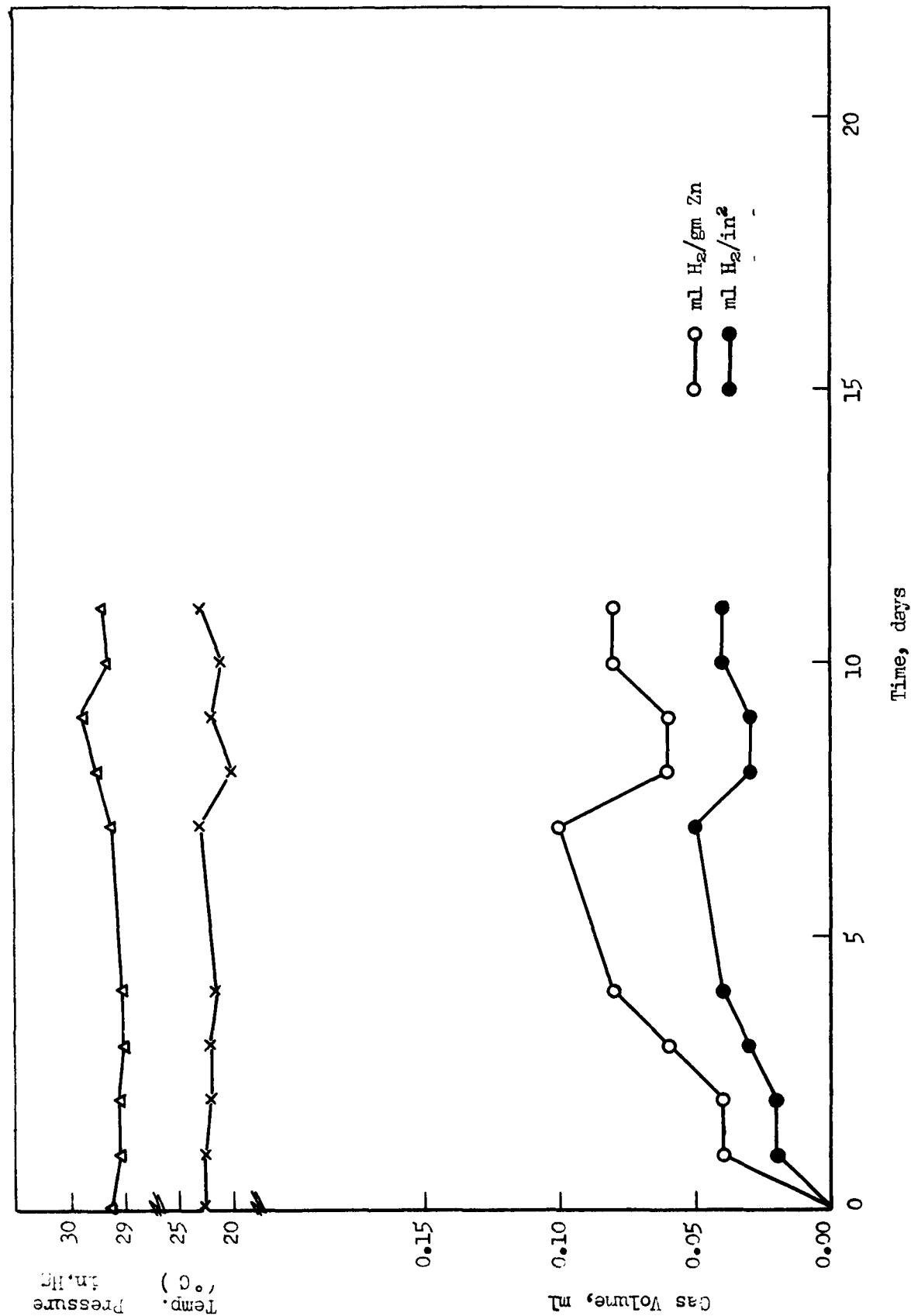


Figure 6 Negative Electrode Chemical Peroxide Rate, 5Zn-95Hg on Silver in 40% KOH-1% ZnO Electrolyte

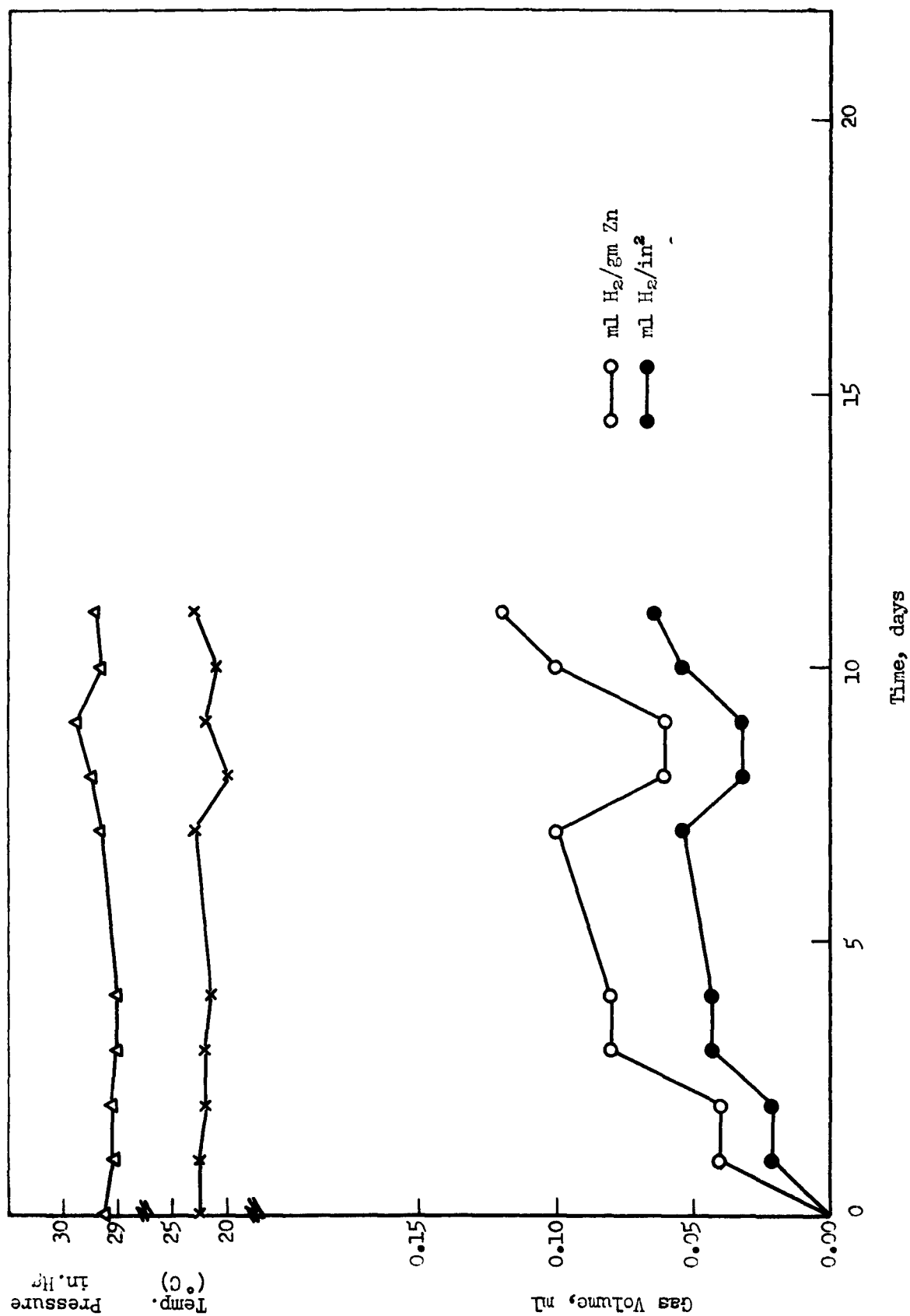


Figure 7 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-2% ZnO Electrolyte

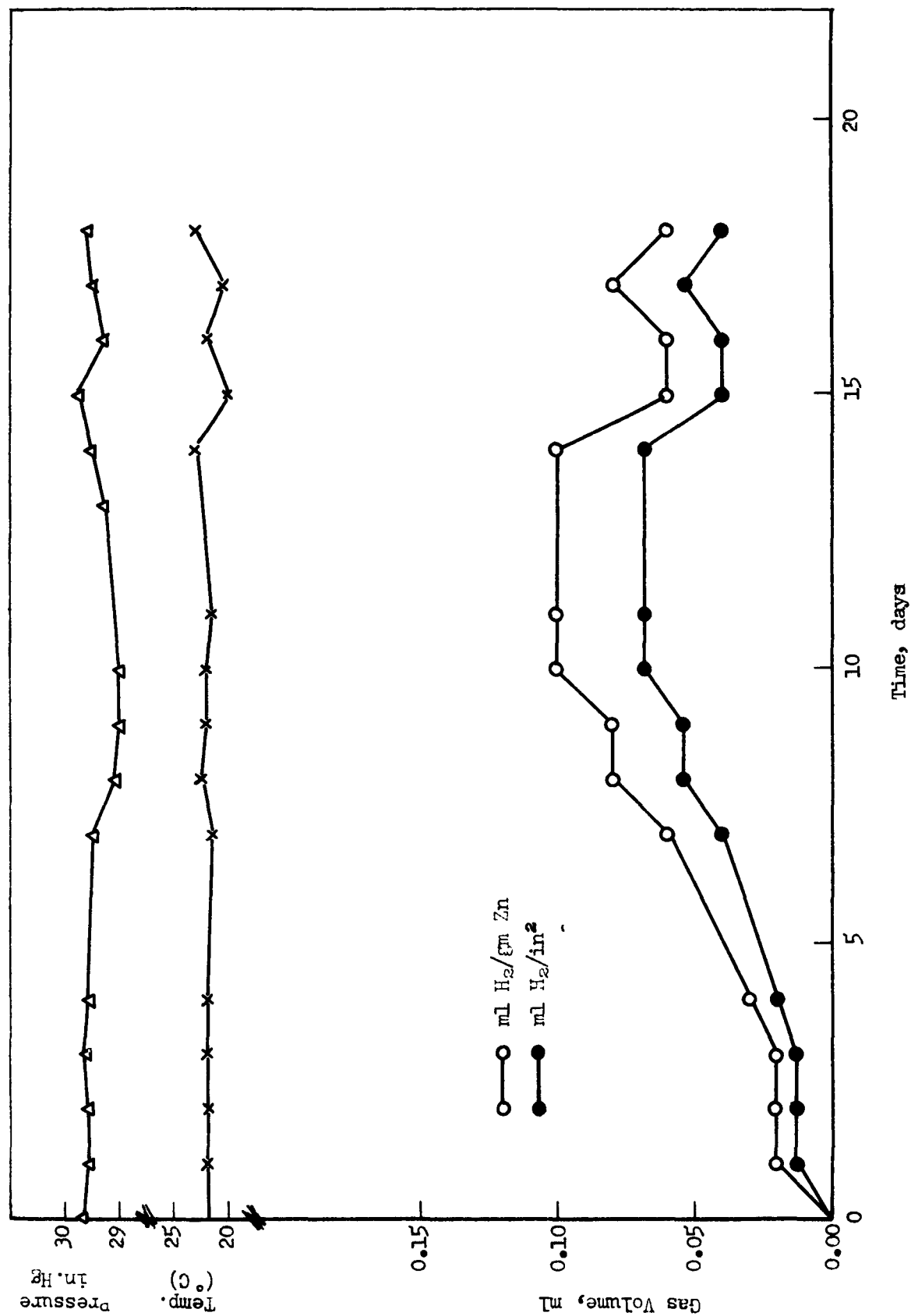


Figure 8 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-4% ZnO Electrolyte

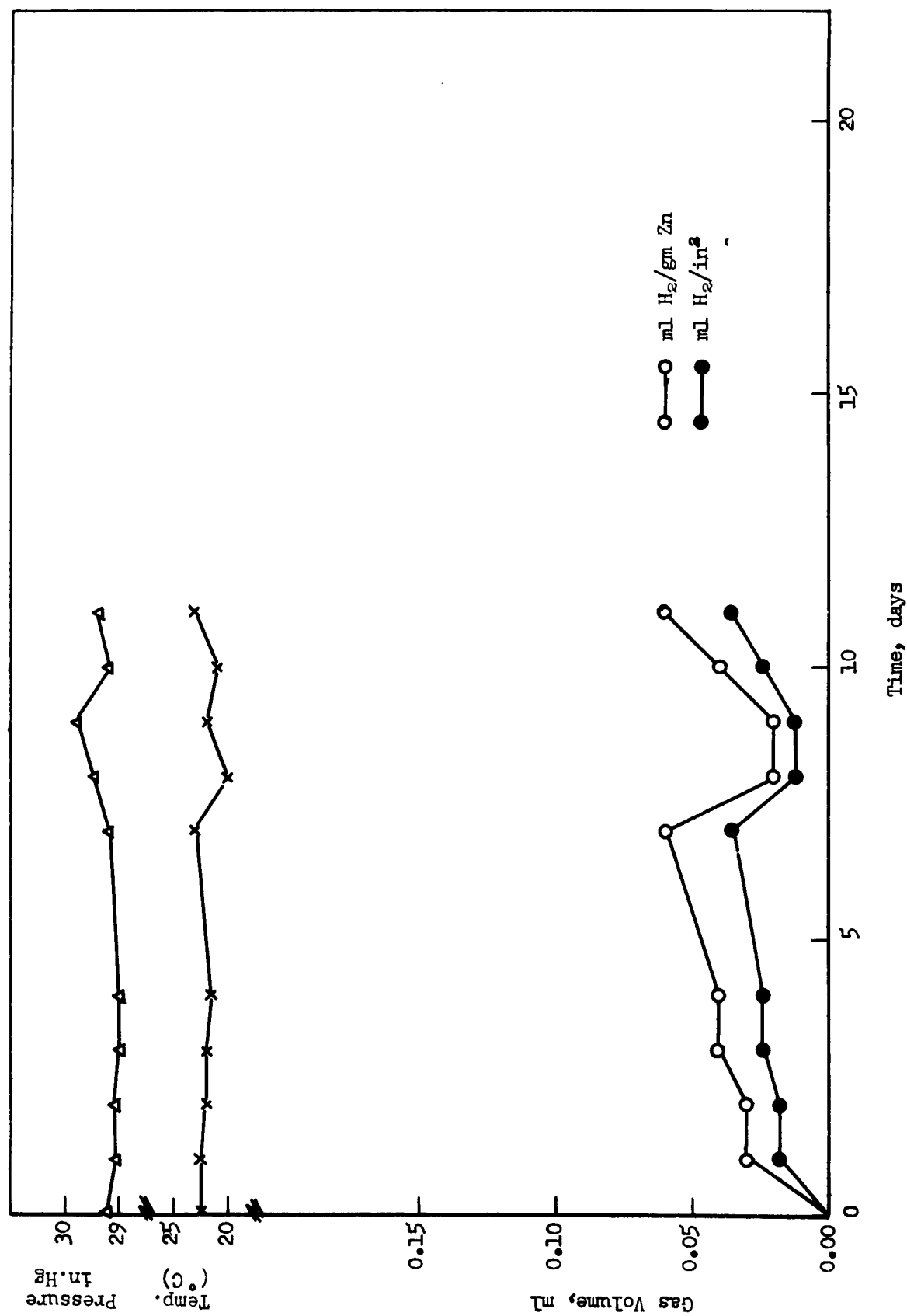


Figure 9 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-6.25% ZnO Electrolyte

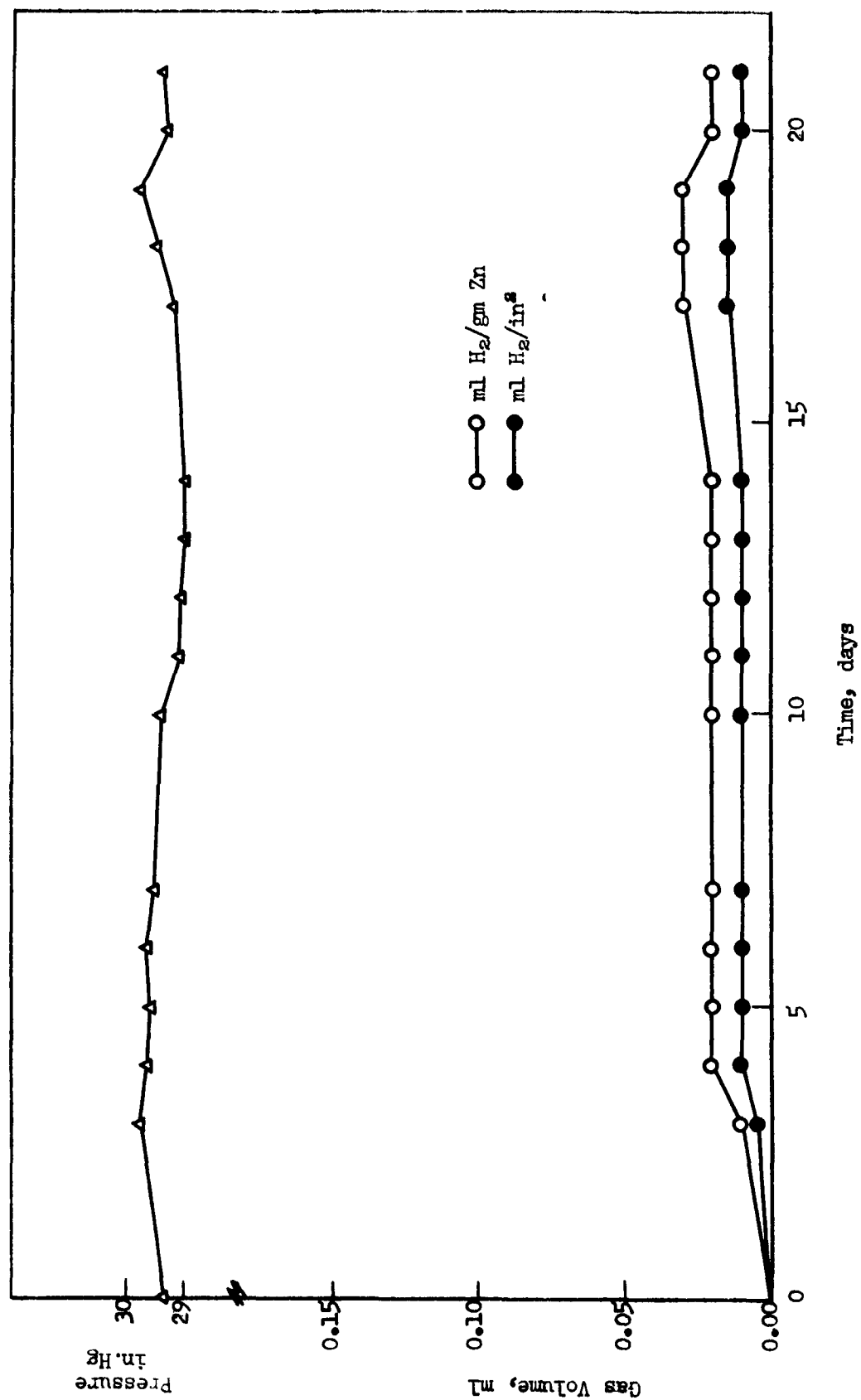


Figure 10 Negative Electrode Chemical Reactivity Rate, 5Zn-95Hg on Silver in 40% KOH-6.25% ZnO Electrolyte at 160°F

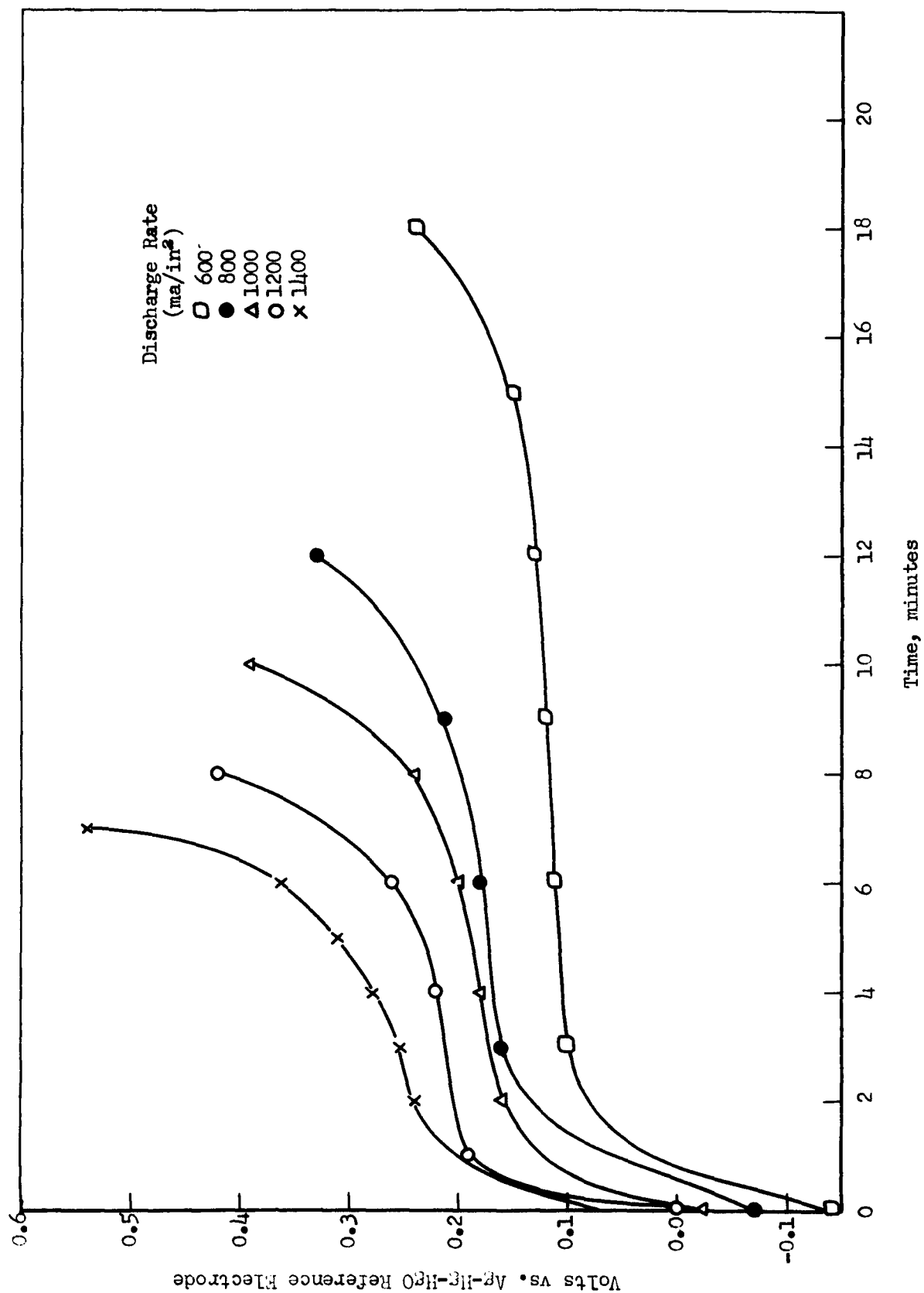


Figure 11 Consecutive Discharges of a Ag-HgO Electrode after a Charge Cycle of 85 Minutes at 128 ma/in²

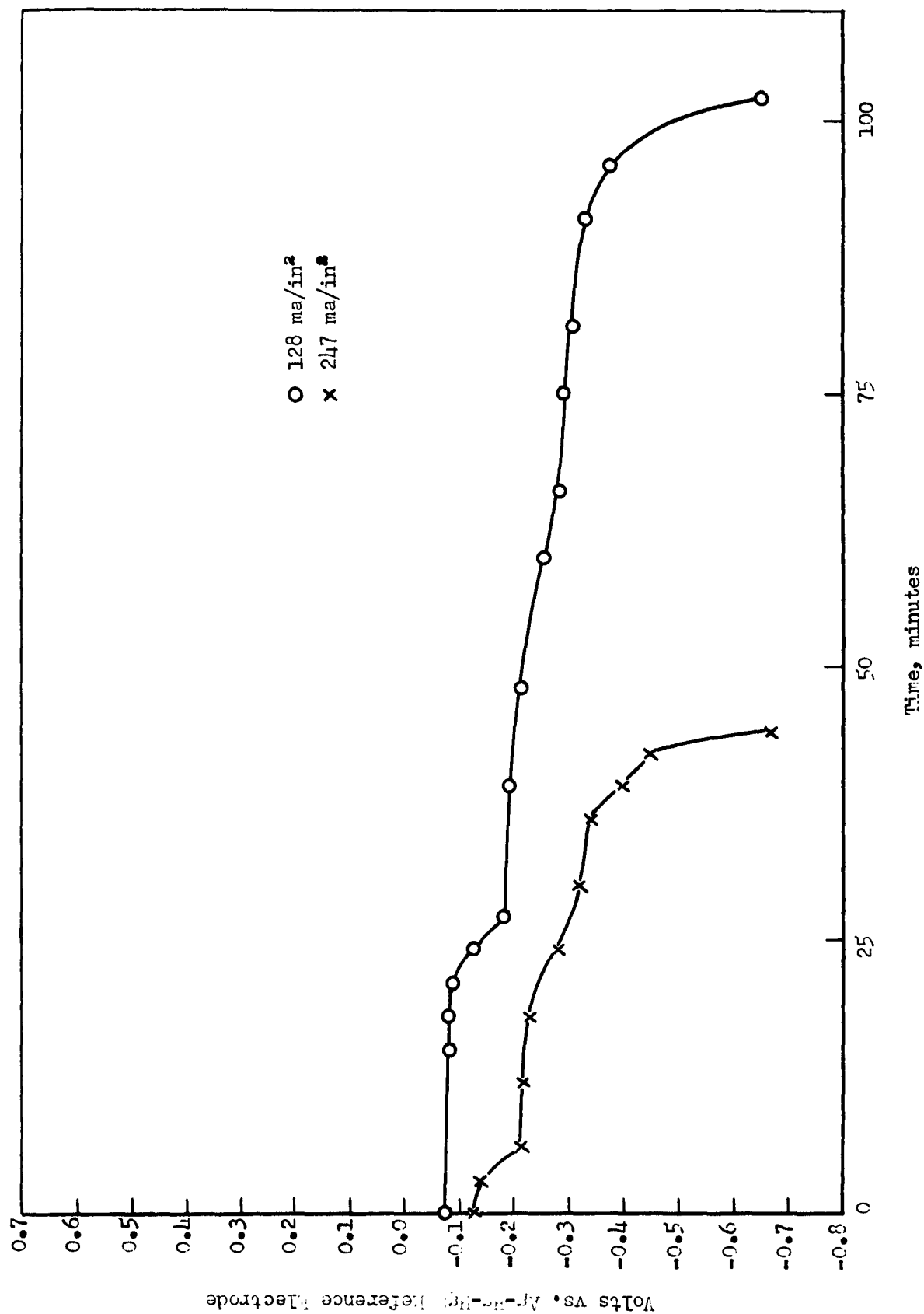


Figure 12 Effect of Increased Charge Rate

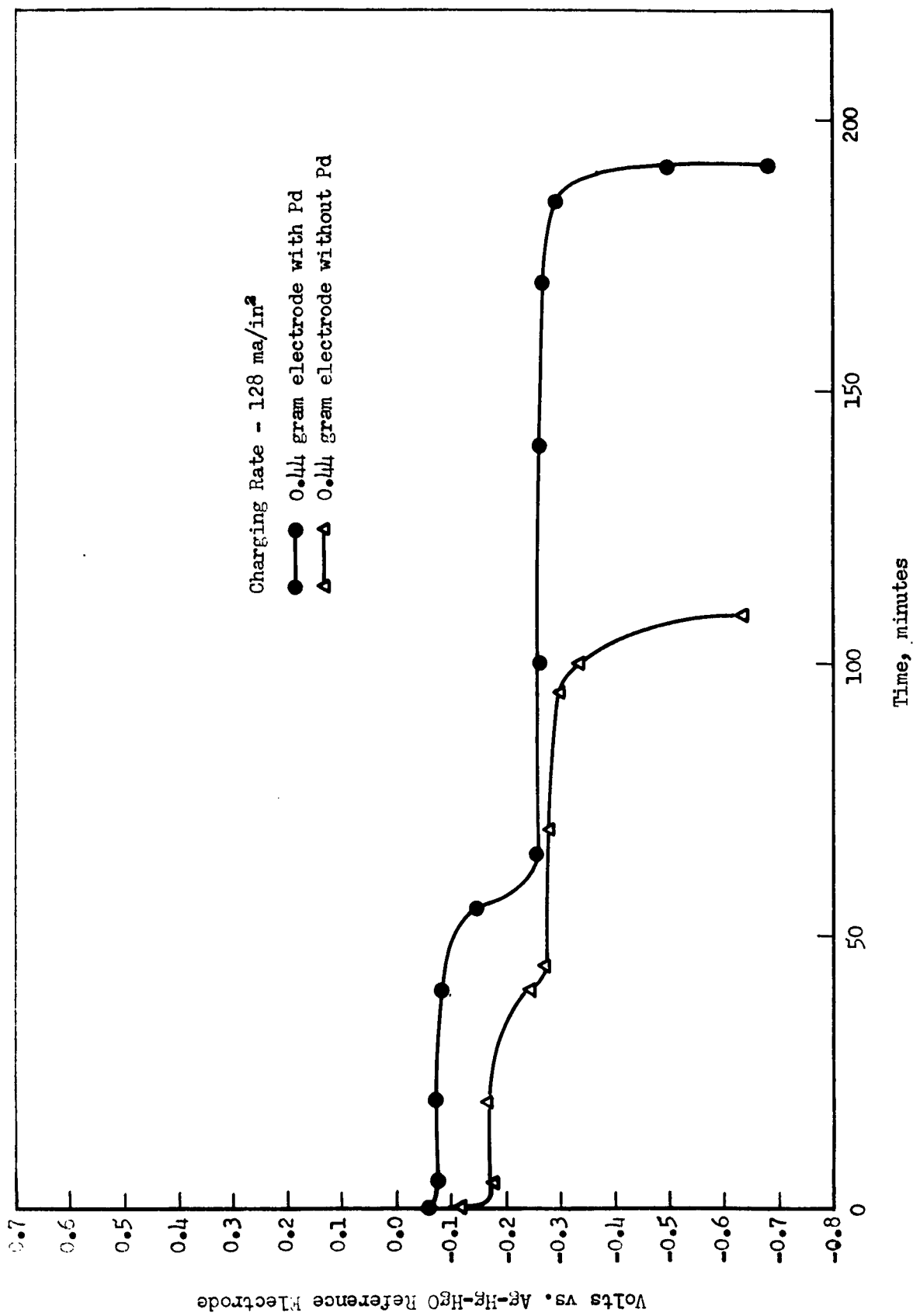


Figure 13 Effect of Palladium in the Positive Electrode

Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

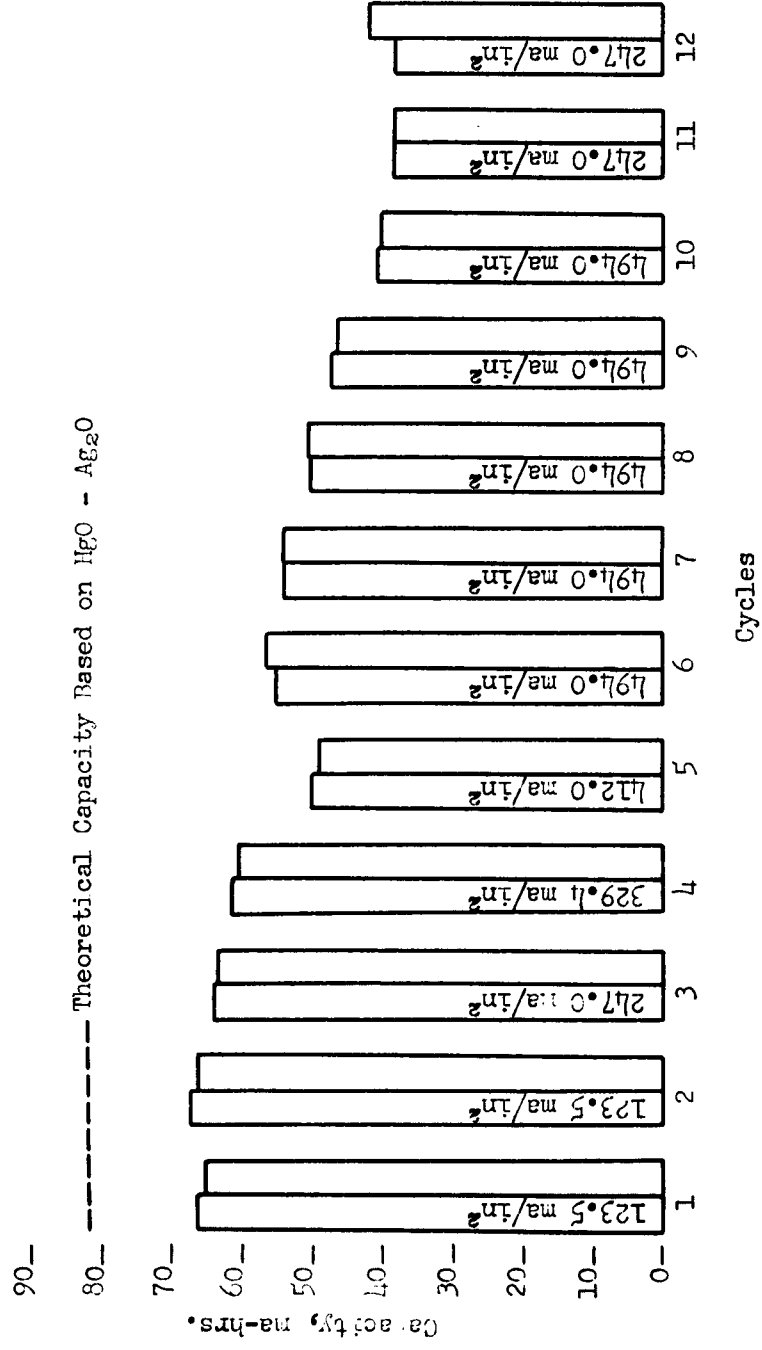


Figure 14 Positive Electrode with 0.3% Pd

Left Bar - Charge(All at 123.5 ma/in²)
 Right Bar - Discharge(at 300 ma/in²).

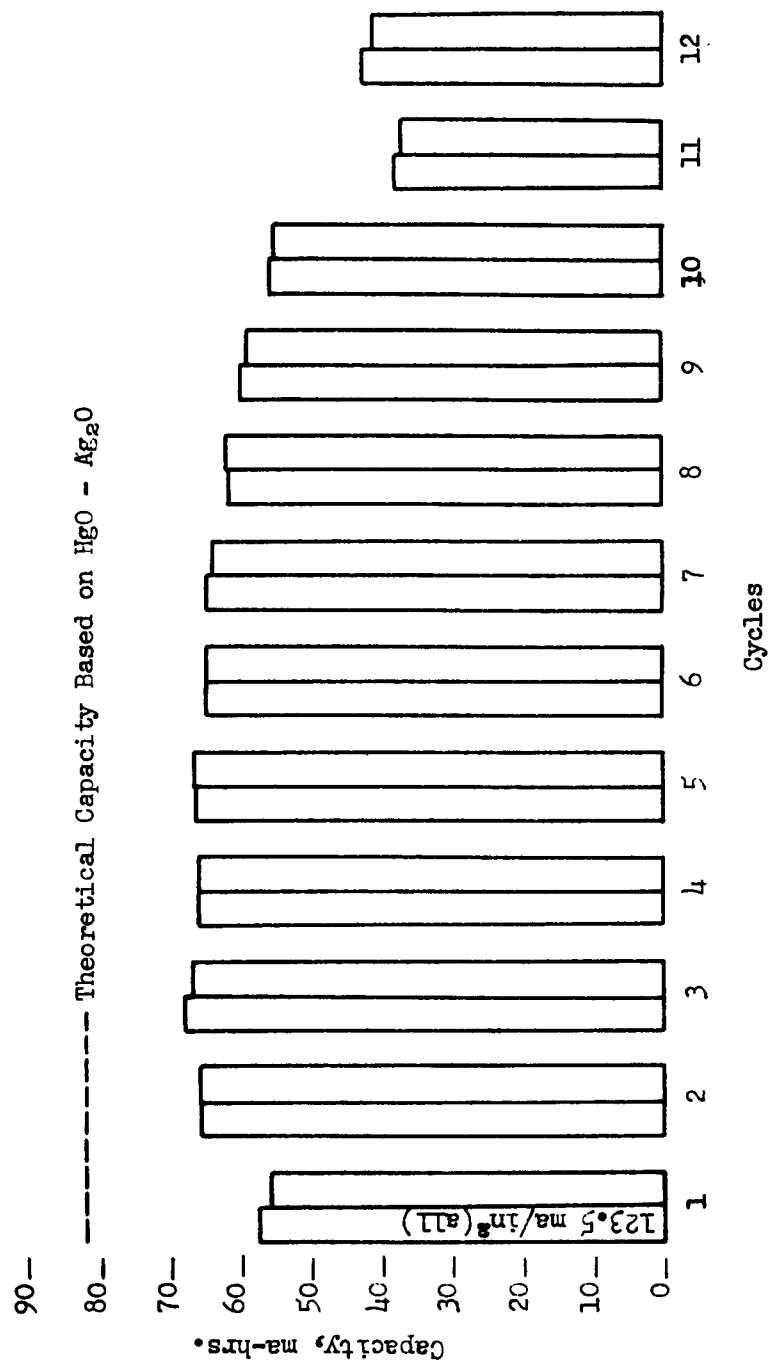
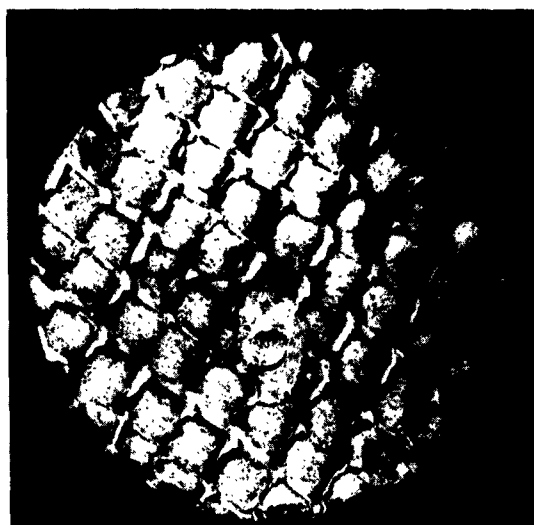


Figure 15 Positive Electrode with 0.3% Pd and 1% Graphite



Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

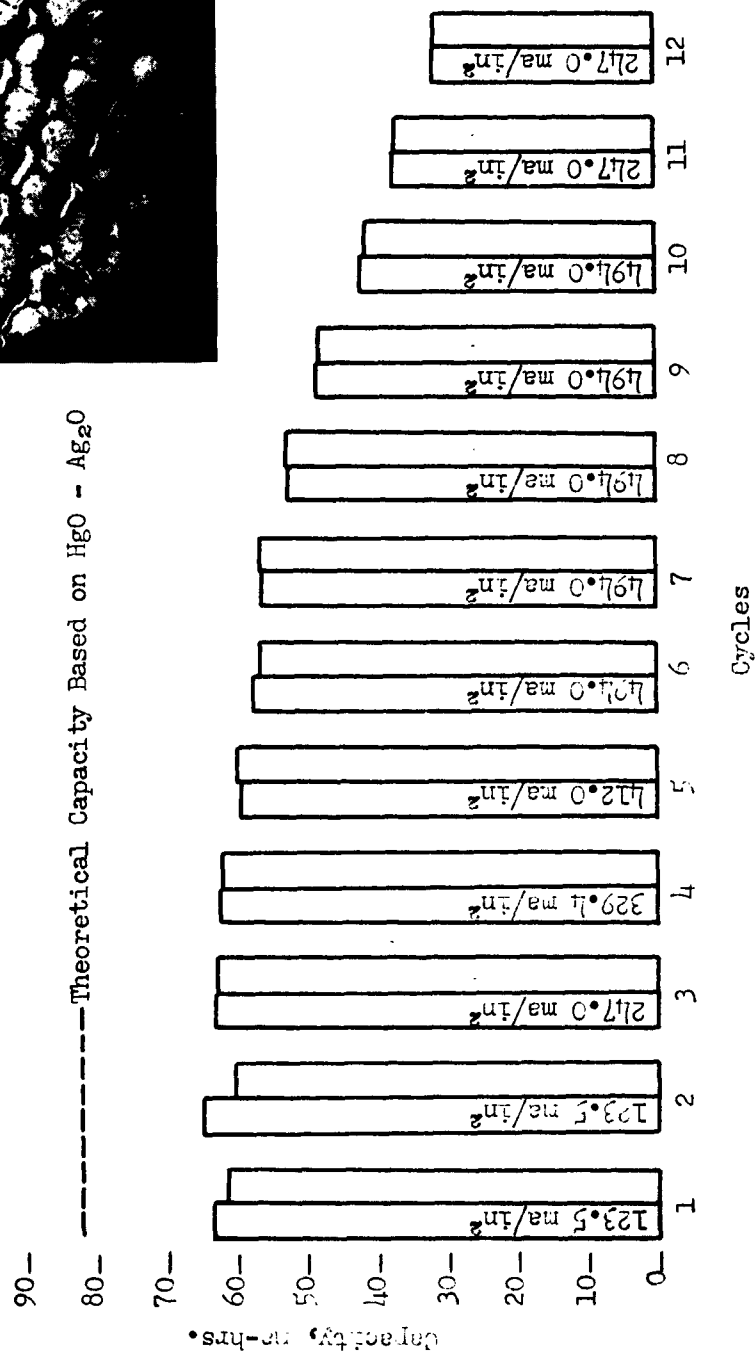


Figure 16 Positive Electrode with 0.3% Pd and 1% Wood Charcoal

Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

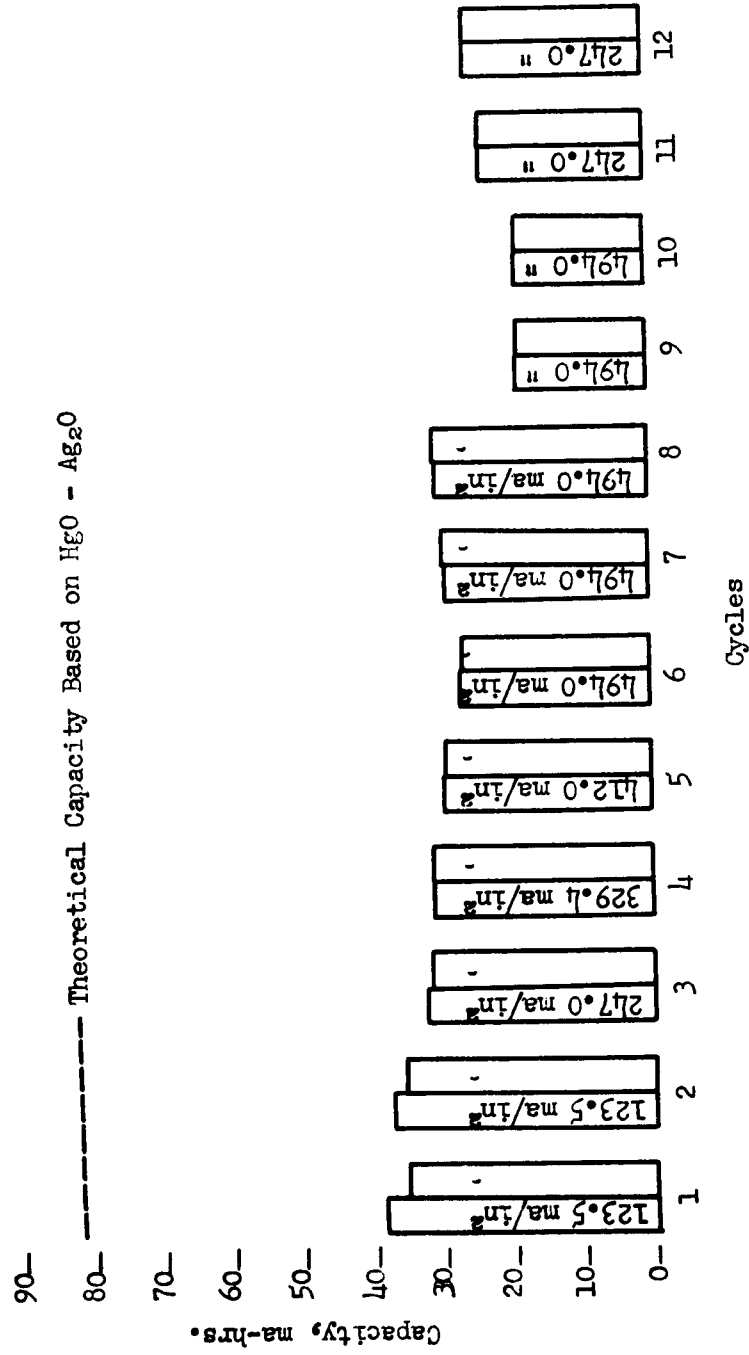


Figure 17 Positive Electrode with 1% Activated Charcoal Containing 10% Pd

Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

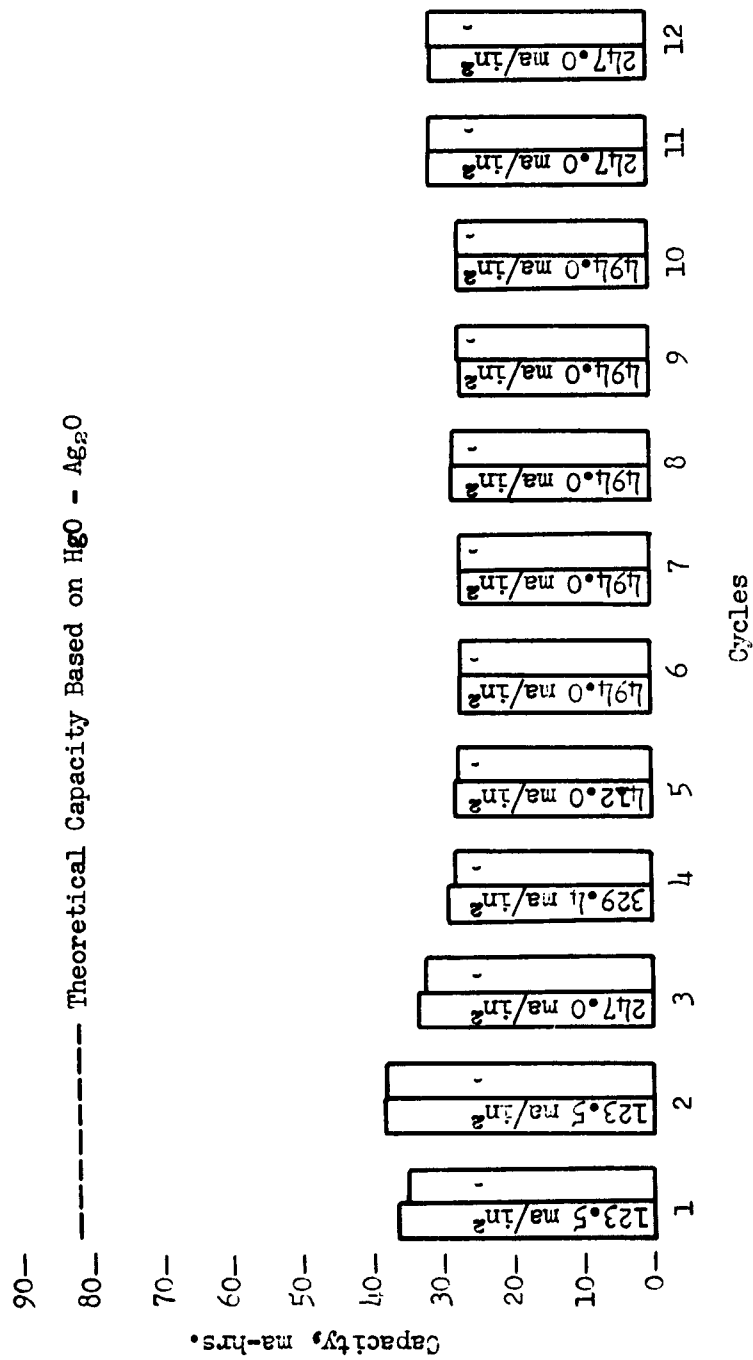


Figure 18 Positive Electrode with 1% Activated Charcoal

Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

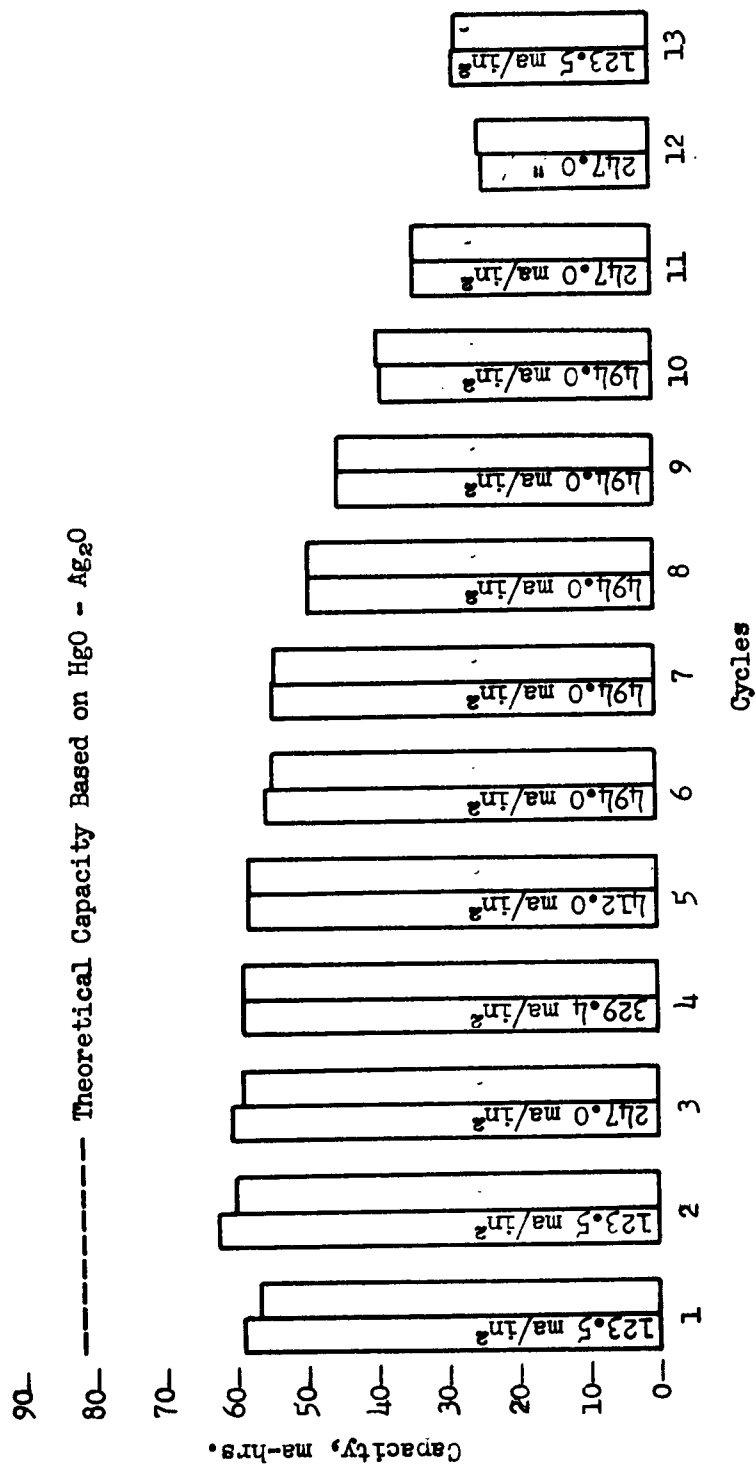
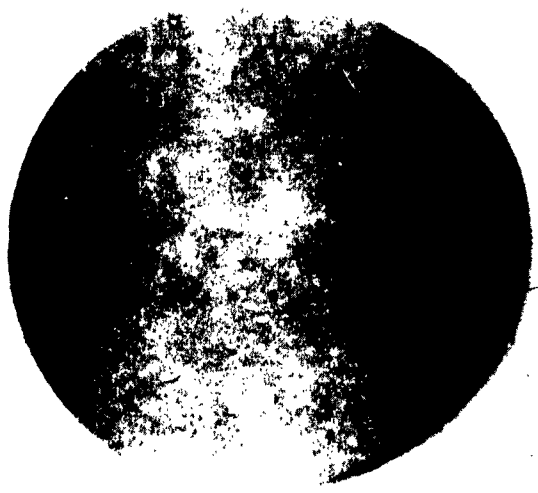


Figure 19 Positive Electrode with 0.3% Pd and 1% Activated Charcoal



Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

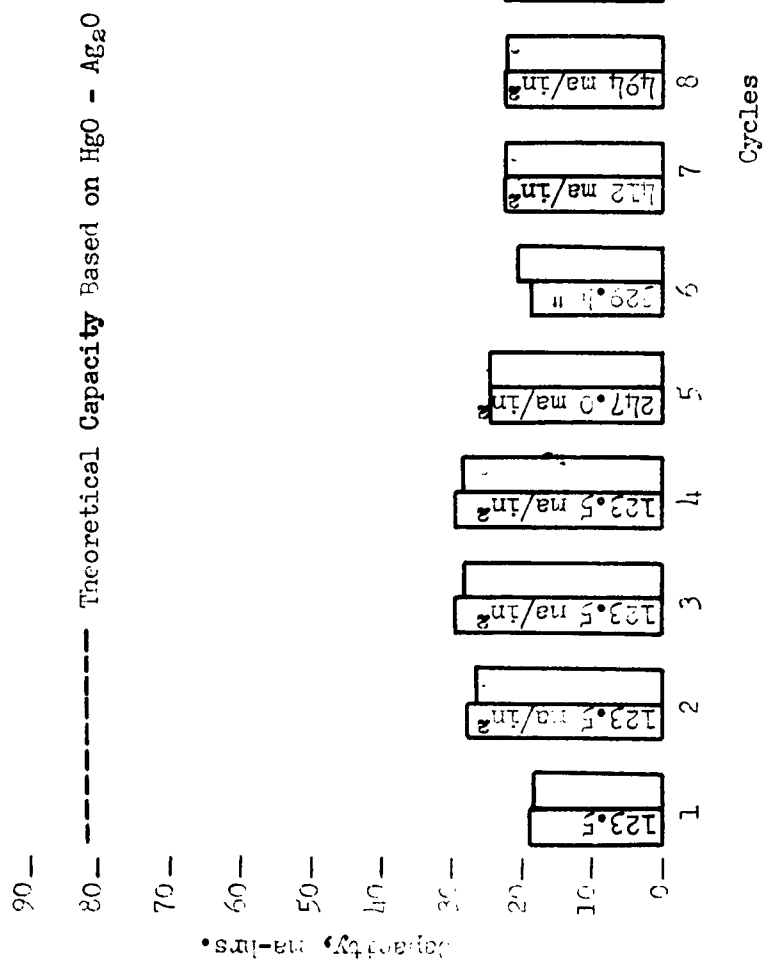


Figure 20 Positive Electrode with 1% Pd and 3% Polyethylene Oxide

Left Bar - Charge
Right Bar - Discharge (at 300 ma/in²)

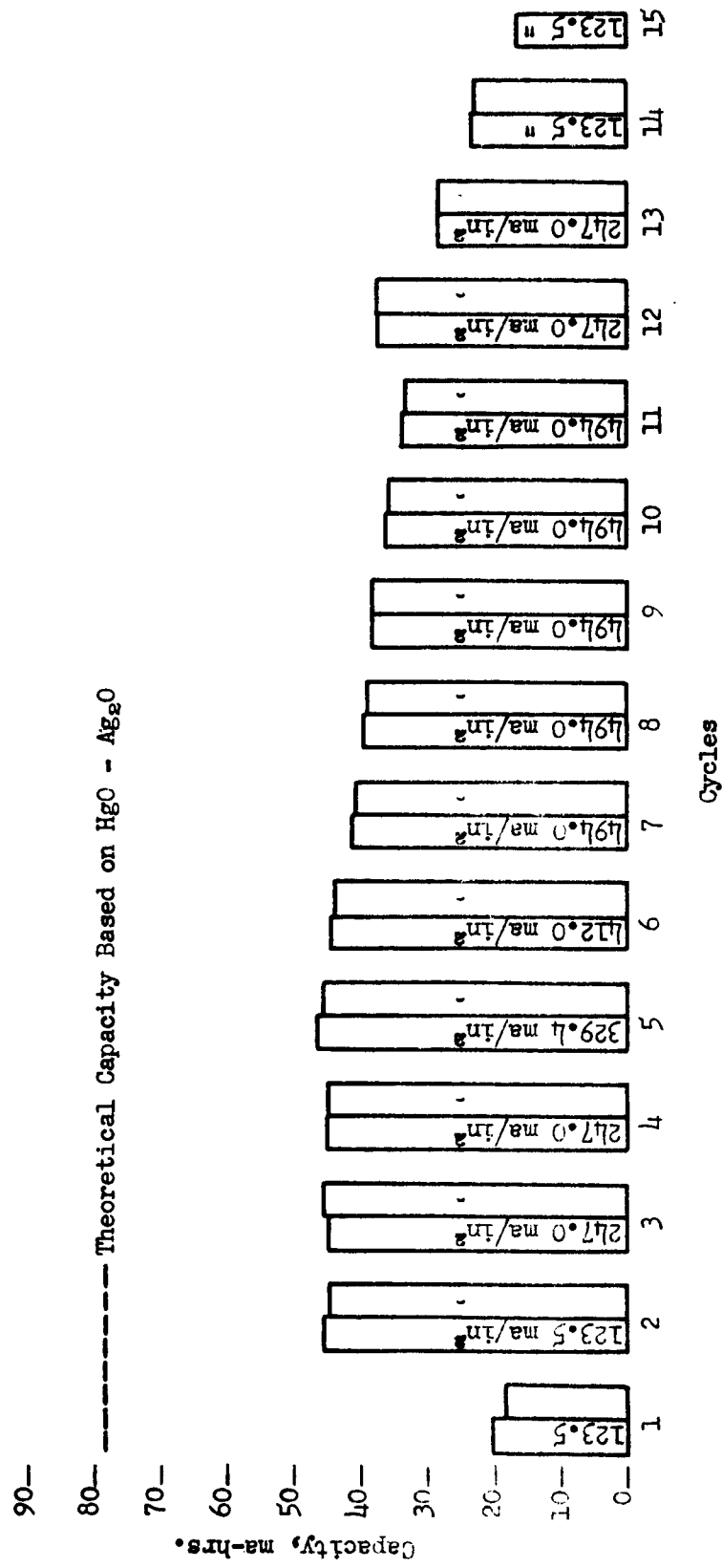


Figure 21 Positive Electrode with 1% Pd-Reduced Particle Size

Left Bar - Charge
 Right Bar - Discharge (at 300 ma/in²)

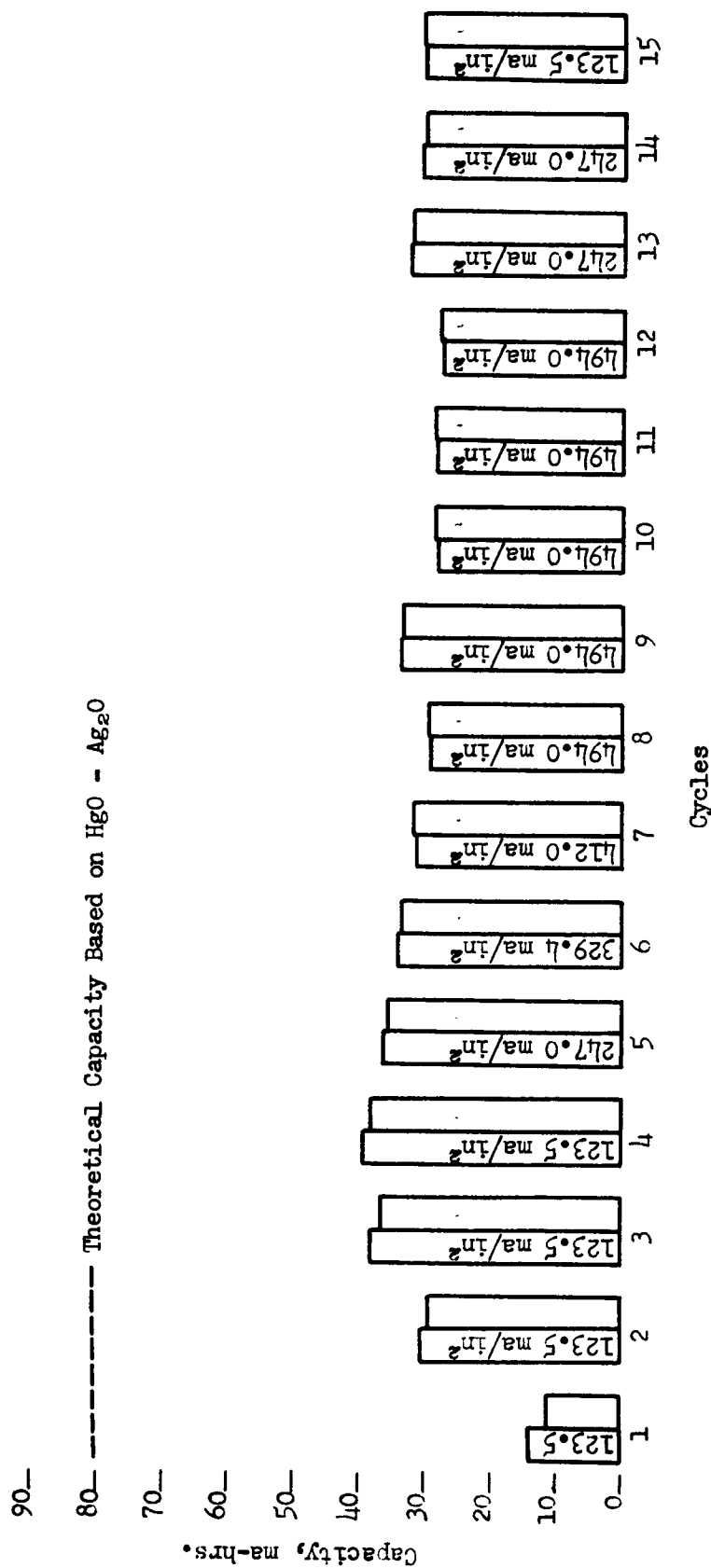


Figure 22 Positive Electrode with 1% Pd and 2% Polyethylene Oxide

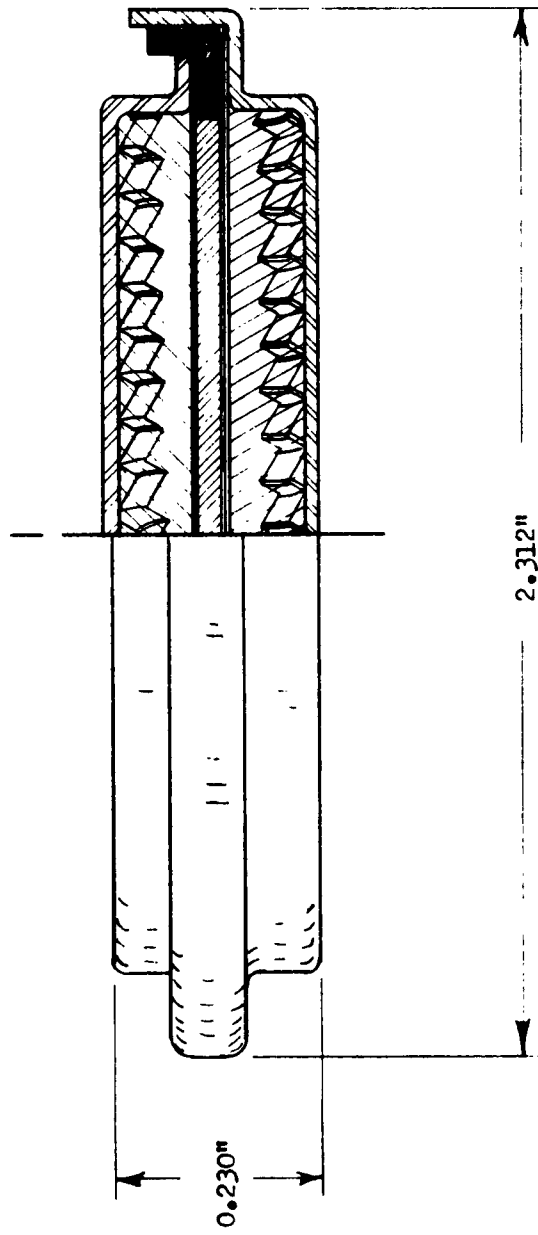


Figure 23 Test Vehicle #2

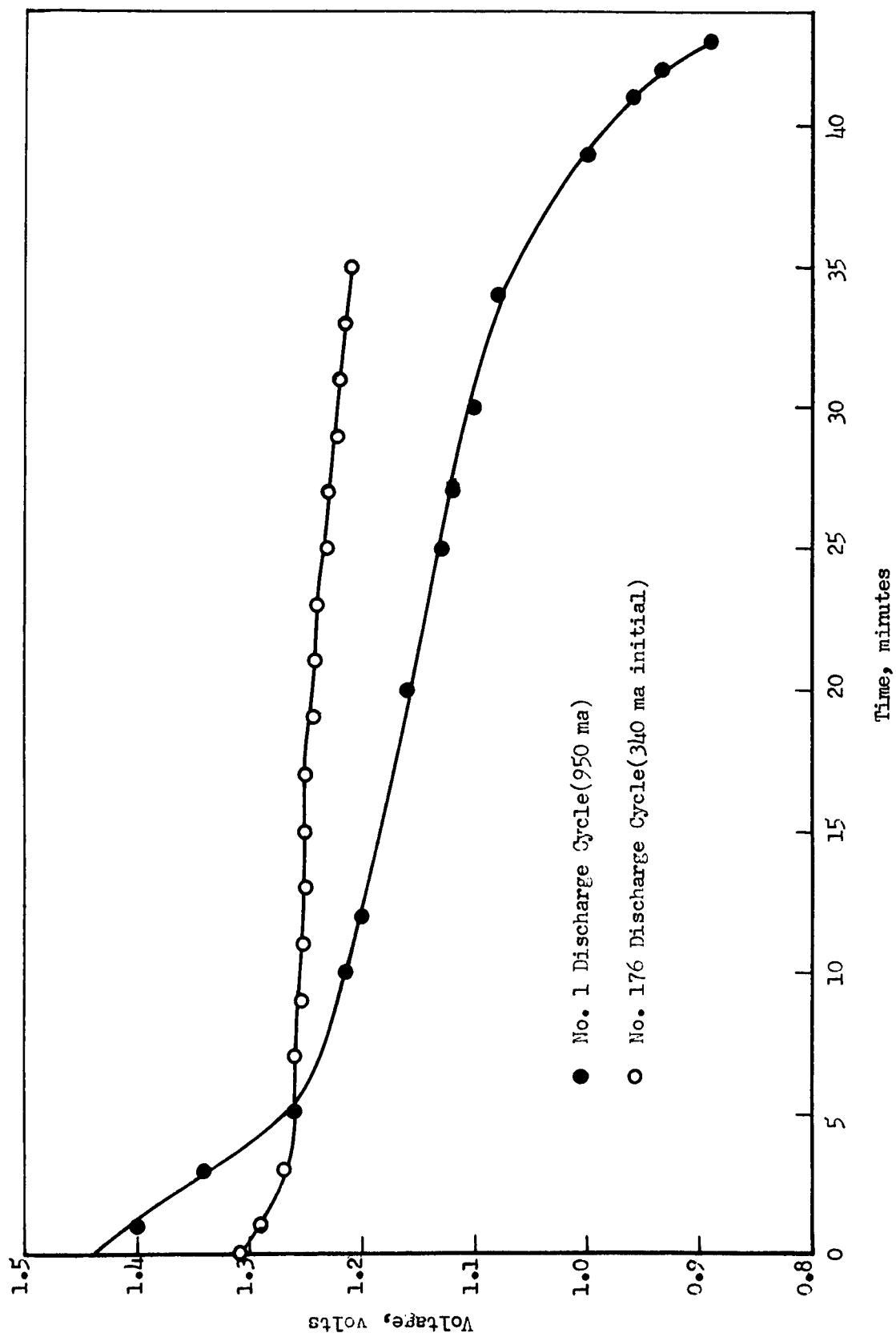


Figure 24 Discharge Curve of Liquid Anode Cell

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The rechargeable electrochemical system Zn/KOH/HgO-Ag has been investigated from the viewpoint of aero space requirements. Individual study phases were used to evaluate cell components. Exploratory research cells were used during positive and negative electrode charge-discharge experiments. Zinc anodes containing high percentages of Hg were discharged with efficiencies over 90% at rates up to 2000 ma/in² under unattended conditions. During chemical reactivity rate studies the system of Zn-Hg-Ag was found to be quite compatible with electrolyte containing zincate. A retaining member for the

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Task 817304-14
II. Contract AF 33(657)-7706
III. P. R. Mallory & Co.
Indianapolis, Indiana
IV. J. M. Boone, R. E.
Ralston
V. Avail fr OTS
VI. In ASTIA collection

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